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# MONOGRAPHS ON INDUSTRIAL CHEMISTRY

Edited by Sir Edward Thorpe, C.B., LL.D., F.R.S.

Emeritus Professor of General Chemistry in the Imperial College of Science and Technology, South Kensington; and formerly Principal of the Government Laboratory, London.

### INTRODUCTION

DURING the last four or five decades the Applications of Chemistry have experienced an extraordinary development, and there is scarcely an industry that has not benefited, directly or indirectly, from this Indeed, the Science trenches in greater expansion. or less degree upon all departments of human activity. Practically every division of Natural Science has now been linked up with it in the common service of man-So ceaseless and rapid is this expansion that kind. the recondite knowledge of one generation becomes a part of the technology of the next. Thus the conceptions of chemical dynamics of one decade become translated into the current practice of its successor; the doctrines concerning chemical structure and constitution of one period form the basis of large-scale synthetical processes of another; an obscure phenomenon like Catalysis is found to be capable of widespread application in manufacturing operations of the most diverse character.

This series of Monographs will afford illustrations of these and similar facts, and incidentally indicate their bearing on the trend of industrial chemistry in the near future. They will serve to show how fundamental and essential is the relation of principle to practice. They

will afford examples of the application of recent knowledge to modern manufacturing procedure. As regards their scope, it should be stated the books are not intended to cover the whole ground of the technology of the matters to which they relate. They are not concerned with the technical minutiæ of manufacture except in so far as these may be necessary to elucidate some point of principle. In some cases, where the subjects touch the actual frontiers of progress, knowledge is so very recent and its application so very tentative that both are almost certain to experience profound modification sooner or later. This, of course, is inevitable. But even so such books have nore than an ephemeral interest. They are valuable as indicating new and only partially occupied territory; and as illustrating the vast potentiality of fruitful conceptions and the worth of general principles which have shown themselves capable of useful service.

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# THE ZINC INDUSTRY

# THE ZINC INDUSTRY

#### BY

### ERNEST A. SMITH, Assoc.R.S.M.,

Deputy Assay-Master, Sheffield; Formerly of the Metallurgical Department of the Royal School of Mines, London; Member of the Institution of Mining and Metallurgy; Member of the Institute of Metals; Member of the Society of Chemical Industry.

WITH 4 PLATES, AND DIAGRAMS IN THE TEXT

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LONGMANS, GREEN AND CO 39 PATERNOSTER ROW, LONDON FOURTH AVENUE AND 30TH STREET, NEW YORK BOMBAY, CALCUTTA, AND MADRAS 1918 LL KB

### PREFACE

ALTHOUGH the art of zinc extraction has been practised in this country for more than a century, comparatively little has been written relative to its development since the publication of the classical work of Dr. John Percy, which appeared in 1861.

It is probably this absence of a special literature dealing with the position of the zinc industry in recent years that partly accounts for the lack of interest hitherto shown in this branch of British metallurgy.

At the present time, however, the importance of the production of zinc and other non-ferrous metals is, fortunately for this country, becoming more generally recognised; it is, therefore, in the highest degree desirable that there should be available treatises suitable for the use of those interested in non-ferrous metals, whether they are manufacturers, users of metals, scientific investigators, or students of metallurgy.

In this work the author has endeavoured to give a general survey of the development of the zinc industry, and its present and possible future position in relation to the various metal industries of this country.

In its preparation the author has freely availed himself of the current literature on the subject. He would more particularly express his indebtedness to the papers by J. C. Moulden, on "Zinc, its Production and Industrial Applications" (Royal Society of Arts, 1916); H. M. Ridge, "The Utilisation of the Sulphur Contents of Zinc Ore"; and also to the Bulletin of the Imperial Institute, 1915–1916, for useful information on the zinc ore resources.

#### PREFACE

Thanks are also due to Mr. Ridge for valuable information and for kindly providing the illustrations of the roasting furnaces, and to Dr. F. C. Thompson for preparing the photomicrographs.

With regard to statistics the figures for the year 1913 have been given purposely in preference to those of subsequent years, as being more representative of the zinc industry under normal conditions. In many cases later figures are not procurable, some of the belligerent nations having ceased to issue them since 1914. Due consideration has, however, been given to the very marked influence of the war on the zinc industry.

A bibliography of some of the more important publications relating to the subject is appended.

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## THE ZINC INDUSTRY

### INTRODUCTION

THERE is considerable truth in the statement, made more than sixty years ago by Dr. John Percy,<sup>1</sup> the father of British metallurgy, that "in proportion to the success with which the metallurgic art is practised in this country will the interests of the whole population, directly or indirectly, in no inconsiderable degree be promoted." This is true, not only of the United Kingdom, but also of the British Empire.

Had the importance of this fact been more fully recognised during the past three or four decades by the Government and by those engaged in the mining and metallurgical industries, there can be little doubt that the valuable mineral resources of the Empire would have been more fully developed and utilised, and adequate provision would have been made for smelting the ores within the Empire in the interests of the metal industries of this country and the Colonies. The crisis through which we are passing has revealed to what an extent our lack of metallurgical enterprise has enabled Teutonic influence to gain control of the mineral and metal resources of the British Empire, and made the United Kingdom largely dependent on foreign supplies to meet her increasing demands for industrial metals.

"Before the war the world's markets for the majority of the non-ferrous metals were very largely controlled by a group of

<sup>&</sup>lt;sup>1</sup> Inaugural lecture to students of the Royal School of Mines, London, 1851.

German metal companies engaged primarily in buying metals and acting as selling agents for producers.

"How complete this control was few people knew. "The outbreak of war disclosed it in all its formidableness.

"The most important of these concerns was the Metallgesell-schaft of Frankfort-on-the-Main. This place was the centre of certain German financial interests which had combined to establish the Metall Bank and the Metallurgische Gesellschaft. In one way or another this great organisation had established financial interests in metal undertakings, not only in Germany and Austria, but also in the United States of America, the United Kingdom, and various parts of the British Empire.

"This enormously powerful group of companies controlled the world's metal markets, of which Frankfort became the centre.

" Their connections with other undertakings and their ramifications were exceedingly complicated and difficult to control. In some instances there was a direct financial connection : in others the connection was established by some form of agreement. But whatever the method, there was no doubt about the ascendency acquired by the Germans."1

In no case was this control more stringent than in that of zinc. Before the war the Germans, by means of the so-called Zinc Convention which they organised, were placed very largely in control of the zinc trade of the world, and were also able to enter into long-date contracts for the supply of large quantities of ore mined within the British Empire, thus placing British consumers of zinc in an unwarrantable position of insecurity.

This control was a source of great embarrassment to the British Government at the outbreak of war, and for guite two years afterwards the cause of this country and its Allies was severely handicapped because we were without the necessary metal supplies, and many trades were in jeopardy. With the view of preventing this control in the future, the Government has recently passed the "Non-ferrous Metals Bill," which is a measure designed to keep the control of the supply of these essential metals in British hands.

For many years the United Kingdom has had to depend on imported metal to the extent of more than 70 per cent. of her zinc requirements.

<sup>1</sup> H. C. H. Carpenter, Nature, 1917, vol. c., p. 284.

Before the war the bulk of the British supply of zinc was obtained from Germany and Belgium. Each country was a large producer of the metal, and each also a large importer of zinc ore from the most important zinc mine in the British Empire, that at Broken Hill, in Australia.

The outbreak of war led to a remarkable situation in the British and Colonial zinc markets, owing to the sudden cutting off of pre-war supplies of the metal, and the loss to Australia of nearly all her markets for zinc ore (concentrates). The demand for the metal increased enormously, zinc as a constituent of cartridge brass being an indispensable munition metal. But whilst there were enormous quantities of zinc ore awaiting shipment in New South Wales, most of the British smelters were unable to treat it, as their furnaces were not adapted to this particular class of ore.

Consequently, at the outbreak of war Great Britain found herself in the anomalous position of having command of the seas, and with an immense supply of zinc ore within the Empire, but with smelting plant quite inadequate to convert this ore into metal.

The serious shortage of spelter was temporarily met by exports from the United States, the world's largest producer of zinc, but as the production in that country is usually only about equal to the consumption, the result was a rapid rise in the price of the metal, the selling price appreciating to more than five times its pre-war figure.

These conditions led to an inquiry into the position of the British zinc industry, and also to a consideration of the possibilities of so increasing the future output of metal that it shall at least be sufficient to meet all home requirements. Such a situation as that in which Great Britain found herself at the beginning of hostilities should never have been allowed to arise, and it is satisfactory to know that steps are being taken to make its recurrence impossible. There is every reason why the supplies of zinc concentrates which have hitherto been largely shipped to the Continent, should be treated within the British Empire, and it is to be hoped that in the future this will be done. Legislation has decided that the resources of the Empire are not, in the future, to be left to be exploited by Germans.

As showing the great importance of the Broken Hill zinc ore deposits it may be stated that the output would be more than sufficient to supply the entire demand of the United Kingdom for metallic zinc.

With the view of relieving the zinc situation and rendering the United Kingdom less dependent on foreign supplies, important schemes, which are dealt with later in this monograph, have been taken in hand, and there seems to be some prospect that the British zinc smelting industry will, in the near future, take the position that its importance demands.

Steady progress has already been made, and the movement is progressing at an accelerated rate, largely through the impetus given to it by the crisis through which the country is now passing.

When the rank this country holds among nations as regards her metal industries is taken into consideration, it must be a matter of surprise that in the past so little attempt appears to have been made to develop the zinc smelting industry so that the production of this important industrial metal shall be commensurate with the needs of the country.

### The Position of Zinc in Commerce and in the Arts

Although zinc was extracted from its ores on a commercial scale in Europe in the middle of the eighteenth century, it did not begin to take a prominent place in the arts until a century later, so that, from an industrial point of view, it is regarded as a comparatively modern metal when compared with metals such as lead and copper that have been in common use for certuries.

Zinc, or spelter, as it is termed commercially, possesses physical and chemical properties that render it extremely useful, and when these properties were fully recognised the metal rose, somewhat rapidly, to a position of considerable importance. It now occupies the third place in the list of non-ferrous base metals of value in the metal industries, only being surpassed in this respect by lead and copper.

The rapidity with which zinc has grown in industrial importance may be judged from the fact that the world's output has almost quadrupled itself in the past thirty years, and in that time the British production has increased tenfold. The world's production of the three non-ferrous metals in most common use in the years 1911-1913—the latest figures available under normal conditions—was as follows :—

#### INTRODUCTION

WORLD'S OUTPUT OF NON-FERROUS METALS.<sup>1</sup>

(In metric tons. 2204.6 lb.)

		Production. Metric tons.	Consumption. Metric tons.	A	vera Pric	
I Lead Copper Zinc	911.  	  1,136,000 893,800 902,100	1,149,200 954,100 911,400	£ 13 56 25	s. 9 1 3	d. 2 9 2
ı Lead Copper Zinc	912.  	   1,181,800 1,018,600 977,900	1,201,800 1,038,700 996,900	17 73 26	15 1 3	10 2 4
I Lead Copper Zinc	913.  	   1,186,700 1,005,900 997,900	1,196,200 1,044,500 1,012,700	18 68 22	6 5 14	2 9 3

From the figures for the production in 1913 it will be seen that for every 1,000 tons of lead produced there were 921 tons of copper and 920 tons of zinc.

This close coincidence between the figures for copper and zinc shows that the relative position occupied by zinc in the arts and commerce was, at the outbreak of war, practically the same as that of copper, a metal which has been in use for industrial purposes for a very much longer period.

Owing to the disturbance caused by the war, it is doubtful how far this ratio is to-day strictly preserved. Zinc owes its important position largely to its valuable pro-

Zinc owes its important position largely to its valuable property of preventing the corrosion or rusting of iron when this metal is coated superficially with it, and also to the fact that it is a valuable constituent of brass, now one of the most widely used industrial alloys.

It may be well here to point out that the nomenclature of zinc is a little confusing. The British usage, and also to a certain extent the American, is to apply the term "spelter" to designate the ordinary ingot zinc of commerce, the word "zinc" being usually reserved for the rolled metal and for chemical and mineralogical terminology.

<sup>1</sup> Statistics issued by the Metall Gesellschaft and the Metall Bank of Frankfort-on-the-Main.

The miner sells ore to the smelter on the basis of its zinc content, and the latter markets the extracted metal as spelter, which is not "a metal" *in sensu stricto*, but a commercial alloy produced by the smelting of zinc ores, and, although consisting mainly of zinc, usually contains sensible proportions of lead and other metals.

Recent usage, so far as Great Britain is concerned, has inclined towards the use of the word spelter for all grades of metal up to those containing 99.8 per cent. of zinc or thereabouts, those of higher quality than this being designated "fine-zinc."<sup>1</sup> Although arbitrary, there are commercial reasons for the distinction.

The crude zinc obtained direct from ores by smelting is usually known in the trade as "virgin spelter" in this country, and as "primary zinc" in America, whereas metal that has been in use and then remelted is termed "remelted spelter" in this country and "secondary zinc" in America.

The term "hard spelter" is given to a cheap and common brand of metal, consisting of zinc contaminated with iron, resulting from the galvanising process.

<sup>1</sup> "Zinc, its Production and Industrial Applications," F. C. Moulden. Journ. Roy. Soc. of Arts, 1916, vol. lxiv, p. 500.

### CHAPTER I

#### THE HISTORY OF ZINC

In turning to the history of zinc it is difficult to determine when, and by whom, the metal was first isolated in the metallic state. Primitive metallurgical processes are referred to in the oldest known historical records, but none of the descriptions of ores and processes used, and of metals obtained, can be applied with any degree of certainty to metallic zinc. Undoubtedly zinc as a distinct metal was unknown in early times, in fact as late as the sixteenth century it was not known in Europe; but there are strong reasons for the belief that the Chinese were acquainted with it as metal at least several centuries earlier.<sup>1</sup>

In Roman times it was known in the alloyed state as a constituent of brass, an alloy of zinc and copper.

Zinc first appears in the coins of the Republic as an impurity; as an intentional addition, however, it only dates from the time of Augustus (20 B.C. to 14 A.D.), when brass was made for the first time in the world's history.

The Romans were the first makers of brass. Although they were unacquainted with the essential constituent, zinc, yet they had discovered that, by melting copper together with a certain ore (calamine, the natural zinc carbonate) by the process known as "cementation," a yellow alloy of a more golden colour than bronze could be obtained, the alloy being known subsequently as "calamine brass." That the Romans were the first inventors of brass is, according to Prof. Gowland,<sup>2</sup> without doubt, as the alloy is not found in Greece or the Greek colonies or elsewhere until the time of the Roman Empire.

<sup>1</sup> W. Gowland, Presidential Address, Journ. Inst. of Metals, 1912, vol. vii, p. 42.

<sup>2</sup> Loc. cit., p. 46.

The first mention of zinc as a distinct metal is usually ascribed to the alchemist Paracelsus (1493–1541), but there appears to be little doubt that it was first actually recognised in the metallic state in Europe by his contemporary, Georgius Agricola, the renowned metallurgical writer, who about the middle of the sixteenth century accidentally discovered it in the wall crevices of a smelting furnace treating zinciferous lead and copper ores at Goslar in the Hartz.<sup>1</sup>

As, however, Agricola only describes the metal and makes no mention of the extraction of zinc from its ores in his well known work "De Re Metallica," 1556, it may be concluded that the metal was not generally known in his time.

The discovery of zinc in Europe seems to have been quite independent of any knowledge of the metal in the Far East, where, as previously stated, it was undoubtedly known prior to the sixteenth century.

There is also some evidence that zinc was known and extracted in India prior to the sixteenth century.

The localities of Eastern production have never been adequately investigated. Nevertheless, it is well known that the Chinese have, from very early times, possessed considerable metallurgical knowledge, and it is not improbable that when the early history of the metallurgy of this ancient people comes to be written it will be found that the first separation of metallic zinc from its ores must be attributed to the Chinese.

There is evidence that the greater part of the zinc produced in the sixteenth and the seventeenth centuries came from China. The metal was imported from China into Europe by Portuguese and Dutch merchants under such names as tutinag, and spiauter, or spialter; hence the word speltrum, introduced by Boyle, and the English word spelter, which is almost the only term for crude zinc in the works at the present day.

The importation of zinc from China has continued to the present day, and quite a substantial quantity of Chinese zinc of very good quality has found its way to England since the war began.

The earliest certain descriptions of zinc production in India <sup>1</sup> For full discussion of the early history of zinc, see Agricola's "De Re Metallica," translated by H. C. and L. H. Hoover, London, 1912, pp. 408-410. appear to be some recipes for its extraction dating from the eleventh to the fourteenth centuries quoted by Praphulla Chandra Rây in his "History of Hindu Chemistry," London, 1902, p. 39. The crude distillation of zinc was conducted in Rajputana as late as the beginning of the nineteenth century, and the remains of such smelting, in this and other districts of India, are said to be very ancient.

### CHAPTER II

#### THE RISE AND PROGRESS OF THE PRODUCTION

### The Establishment of Zinc Smelting Centres

WHATEVER uncertainty there may be as to the antiquity of the discovery of metallic zinc, there appears to be little doubt that the art of extracting it from its ores by distillation was acquired from the Far East and was introduced into Europe in the latter part of the eighteenth century.

There is a tradition, recorded by Bergman, that an Englishman visited China in the eighteenth century expressly to learn the method of making zinc; that he attained his object and returned home in safety with the secret; and that some time afterwards works were erected at Bristol for the extraction of zinc in large crucibles by distillation *per descensum.*<sup>1</sup> This tradition is supported by the fact that zinc works were established at Bristol about 1740, by John Champion, who was, so far as is known, the founder of the British spelter industry, and also the first metallurgist in Europe to extract zinc from its ores commercially. Exactly what circumstances led Champion to start the spelter industry at Bristol must be more or less a matter of conjecture, but probably it was due to the fact that a calamine-brass industry had been in existence in England for about a century previously.

Formerly calamine, an important ore of zinc, was fairly abundant in England and was employed in brass-making, and was also exported as ballast to the Continent to be used for the same purpose. It is recorded that calamine-brass works were erected in Surrey about the middle of the seventeenth century. Works were also established in Bristol about 1702, and after-

<sup>1</sup> Quoted by J. Percy, "Metallurgy of Copper and Zinc," London, 1861, p. 520.

wards at Cheadle, in Staffordshire, about 1720. Later, works were erected for the manufacture of ingot-brass at Smethwick, Swansea, and Llanelly.

The smelting of zinc ores was continued at Bristol for nearly one hundred years, when it was transferred to Swansea, which possessing greater natural facilities for the development of the industry, gradually became the most important centre of zinc production in the United Kingdom.

The manufacture of brass by cementation was also carried on in Europe in the eighteenth century, notably at Moresnet in Belgium, and at Beuthen in Poland, at which places important deposits of calamine (zinc carbonate) were worked. As the art of zinc smelting gradually became known, it necessarily followed that in course of time it should be introduced at these noted European centres of brass-making. It was not, however, until some fifty years after the establishment of the industry in England that it was introduced on the Continent.

The manufacture was started in Germany about 1798 by Johann Christian Ruberg, who probably learned it in England, and began zinc distillation at the glass works of Wessola, near Pless, in Poland.

Ruberg first adopted the method of distillation *per descensum* as practised at Bristol, but he soon found that it was very defective, and devised the system of treatment in horizontal muffles of large capacity, known as the Silesian method. Ruberg thus laid the foundation of what became, in later times, the important Silesian zinc industry.

About the same time, zinc distillation from calamine was also started at Dollach, in Carinthia, by Dillinger, by the method practised at Bristol, but the works only remained in operation for a comparatively few years.

The calamine deposits at Moresnet, in Belgium, passed in 1795 under the suzerainty of France, and it is stated that the Government in granting a concession of mining rights to the Abbé Dony, imposed on him the obligation to make such experiments as would enable the calamine to be reduced to the metallic state. Whatever truth there may be in this story, the introduction of zinc smelting into Belgium is to be credited to the Abbé Dony, who, after many years of experimental work, appears to have made the independent discovery of a method of zinc distillation and to have established works at Liége in 1807. These works formed the corner-stone of what became in later times the world-famed Belgian zinc industry. They have for many decades outlived the native supply of zinc ores on which, with the presence of coal of the district, the industry originally depended.

Subsequently, works were established at Moresnet, near Aix-la-Chapelle, to smelt the important deposits occurring at La Vieille Montagne, La Nouvelle Montagne, and Corfalie.

Dony's method of zinc extraction differed from that employed in Great Britain and in Silesia. He distilled the calamine in a number of small retorts set in a single furnace, thus constituting the Belgian method, adopted by all the Beigian zinc works erected later, and subsequently in England and elsewhere. Dony reaped little benefit from his discovery; he died a ruined man in 1819, and his successor, M. Dominique Mosselmann, who was admitted as Dony's partner in 1816, took over the works. Although a man of great energy and capability. Mosselmann had not brought about any noteworthy progress in the zinc industry when he died in 1837, possibly because up to that time no regular demand had been found for the increasing output of this new commercial metal.

Mosselmann carried on the works until his death, when his successors, in order to realise his estate, founded the celebrated Société de la Vieille Montagne, with a capital of 7,000,000 frances (£280,000).<sup>1</sup>

The growth of the company was at first very slow, and it was only when Saint Paul de Sincay took over the management that the works began to prosper rapidly. By the middle of the nineteenth century the Belgian industry

By the middle of the nineteenth century the Belgian industry had become firmly established, and was a formidable rival to that of Germany in the amount of zinc produced annually. Both Belgium and Germany adopted the method of zinc distillation *per ascensum*, which proved to be more economical and more satisfactory than distillation *per descensum* as used in England.

The latter method, which was also carried on to a limited extent in Carinthia and Hungary, was discarded in England in favour of the former method about the year 1850.

Towards the latter half of the last century zinc smelting was also started in Austria, Holland, Spain and France, but the

<sup>&</sup>lt;sup>1</sup> J. Gilbert, The Mining Journal, London, 1916, vol. cxiv, p. 480,

industry in these countries has never grown to very large proportions, the production, even at the present time, being insufficient to satisfy their own requirements.

During the eighteenth century the growth of the European zinc industry was comparatively slow, owing most probably to the somewhat limited use of the metal at that time in the manufacture of brass. Although Emerson used metallic zinc for the manufacture of brass in England as early as 1781, its use for this purpose extended very slowly owing to the indifference, and even hostility, displayed by the calamine-brass makers, who averred that the metal produced brass inferior in quality to that produced by cementation.

The long survival of this ancient process, after the discovery of metallic zinc, and its production on a commercial scale, afford a striking example of the conservatism characteristic of early British metallurgy.

At the beginning of the nineteenth century it was found to be possible to convert zinc into sheets by heating it to a temperature between 100° C. and 150° C. and rolling it while hot, thus breaking down the crystalline structure of the metal, and rendering it malleable and ductile.

The credit of this discovery is due to Hobson and Sylvester, of Sheffield, who in 1805 obtained a patent for "a method of manufacturing the metal called zinc into wire and into vessels." This discovery was of no little importance, as it enabled the metal to be used for the manufacture of sheets for roofing purposes, for which the higher priced metal, copper, had hitherto been employed.

Very little advantage appears to have been taken of the patent in this country. The Abbé Dony, however, laid down the first rolling mills for sheet zinc production at Liége in 1812, and since that time the manufacture of zinc sheets has been a very important branch of the Belgian zinc industry.

The initial difficulties of finding a suitable outlet for the increasing quantities of the zinc produced at the different centres of production lasted over several decades.

As late as 1825 the association for fostering the Prussian industry offered a prize for the discovery of a useful employment of zinc, and this led to its use for ornamental purposes, as imitation bronze for statues, lamps, pedestals, and for architectural pieces, etc. Further impetus was given to the zinc industry by the employment of the metal for the manufacture of the so-called "galvanised" iron, the name given to sheet iron coated superficially with zinc to prevent its corrosion when exposed to atmospheric influences.

The term "galvanised" is said to have been first used, improperly, in France and subsequently adopted in this country.

The galvanising process is effected by dipping the iron articles into a bath of melted zinc, a patent for zincing iron in this way being granted to H. W. Crawford in 1837.

The application of these two valuable properties of zinc greatly extended its use for industrial purposes when once their importance was fully realised.

It was not, however, until the middle of the nineteenth century that the zinc industry began to be established on a sure footing in Europe. In 1830, the total production of spelter in Europe was less than 5,000 tons, and in 1840, ten years later, the total output had only reached a little more than 17,000 tons.

From this time onwards, however, there was a steady increase in the production of the metal, until it eventually occupied third place in the list of non-ferrous metals of industrial importance A notable increase in output occurred from about 1873, due to the progress of galvanising.

Zinc smelting was not introduced into America until 1838, in which year the metal was first produced experimentally in the United States. Between the years 1841 and 1850 various attempts were made to smelt the red oxide ore of New Jersey, which is contaminated with willemite and franklinite in such a way that a clean separation could not at that time be economically effected.

The attempts to produce metallic zinc were unsuccessful, and attention was then directed to the recovery of the zinc as oxide, and works for the manufacture of zinc oxide on a commercial scale were erected in Jersey City in 1854.

The regular production of metallic zinc was not undertaken until 1859, when J. Wharton started zinc smelting in muffle furnaces of the Belgian type, with Pennsylvanian anthracite as fuel.

By 1870, six works were producing zinc in the United States at the rate of approximately 4,500 tons per annum, while the works in New Jersey produced in addition about 13,000 tons of zinc oxide.

### THE RISE AND PROGRESS OF THE PRODUCTION

While at this time the American industry was only just becoming established, the European industry had made considerable progress, as shown by the following figures giving the approximate zinc output for the various countries of Europe in 1870:—

						L	ong tons.
Germany				••		••	56,000
Austria	••		• •	••	••	••	3,000
Belgium	•••		••		••	۰.	46 <b>,0</b> 00
Great Bri	tain	(estimat	ed)	••	••	••	10,000
France			••	••	••	••	6,500
Spain		,,	••	••	••	••	6,500
Total E	uroj	pean zind	prodi	uction i	in 1870	••	128,000

This amount, with 4,500 tons of spelter produced in the United States, makes a total of approximately 133,000 tons as the world's zinc production in 1870. The production of the individual countries in recent years is dealt with on page 158.

Attention must be directed to the fact that although domestic ores were mined and smelted in Europe at this time, a by no means inconsiderable quantity of imported zinc ore was also smelted. Thus, the total annual production of the famous zinc ore in the island of Sardinia was, in 1870, about 49,200 tons, representing 16,900 tons of zinc; this ore was chiefly exported to Germany, Belgium, and the United Kingdom.

The enormous increase in the rate of production, and in the demand for zinc since the year 1870, is well shown in the following figures, which give the approximate output and consumption of zinc, in English tons from 1870 to the outbreak of war, in intervals of ten years.

	Year.		European production.	American. production.	World's production.	World's consumption.			
			English tons, 2,240 lb.						
1870 1880 1890 1900 1910 1913	· · · · · · · · ·	· · · · · · · · ·	128,000 207,000 310,000 557,000* 663,000*	4,500 21,000 58,000 247,000 315,000	133,000 228,000 343,000 368,000 804,000 982,000	230,000 345,000 474,000 820,000 997,000			

\* Includes small amounts produced in Australia.

It will be seen that not only has there been an enormous increase of production, especially during the present century, but the ratio between the European and the American production has altered, implying far-reaching economic changes in regard to the supply and demand for zinc.

The increase in the world's supply of zinc from 1845 to 1913, in English tons, has been plotted graphically by J. C. Moulden in the accompanying curve (page 17). Prior to 1845, the statistics are not very trustworthy, and in any case the tonnage was so small as to have little bearing upon the metal in relation to the part it plays to-day in our commerce. The curve indicates in a striking manner the ever-increasing relative rate of production, a considerable advance being noted about 1873, due to the progress of galvanising. With the exception of a decrease in 1900 and 1908, there has been progressive output, the increase for 1900 to 1913 being very remarkable. In the relatively short space of sixty-eight years the world's output has increased about 3400 per cent. (Moulden). The actual figures compiled by Moulden for the world's zinc production for the period included in the curve 1845-1913 are as follows (in English tons) :—

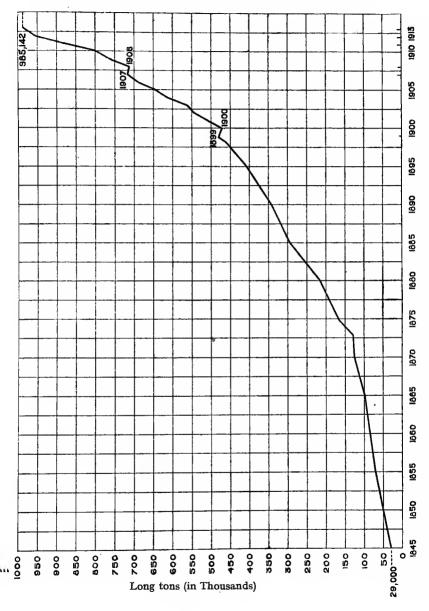
Year.	English tons of 2,240 lb.	Year.	English tons of 2,240 lb.
1845	29,000	1904	612,687
1855	70,000	1905	643,906
1865	98,000	1906	688,321
1875	166,000	1907	725,616
1885	294,000	1908	711,514
1890	342,000	1909	762,559
1895	406,000	1910	797,336
1900	471,460	1911	880,411
1901	508,422	1912	955,398
1902	544,193	1913	985,142
1903	561,547		

Тне	World's	PRODUCTION	OF	Zinc.1
	From	1845 to 1913		

A significant feature of the zinc industry is its limitation to the comparatively few smelting centres in Europe and America

<sup>1</sup> Compiled by J. C. Moulden, Journal of the Royal Society of Arts, 1916, vol. lxiv, p. 527.

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already mentioned, viz.: Silesia, Westphalia and Belgium on the Continent; Swansea, Birmingham, and more recently Durham in England; Kansas, Illinois and New Jersey in the United States. In recent years, a zinc smelting plant, to which reference will be made later, has been erected at Port Pirie in Australia. These are the more important smelting centres contributing to the world's supply of zinc, and to one or other of these centres practically all zinc ores have, hitherto, been shipped for treatment.

This localisation of the zinc industry is due to the necessity for cheap fuel, the occurrence of good quality fireclay required for the retorts used in smelting, and to the necessity of skilled labour, whilst the climatic conditions must be suitable to the trying conditions of the workers.

It has been found very difficult to install zinc smelting works without close regard to these somewhat narrow factors; in regard to labour especially, it takes many years to train the workers, whose skill and practical knowledge may be said to result from environment and in this branch of operative metallurgy to become almost hereditary.<sup>1</sup>

The main strength of the great centres of zinc production to-day may be said to be their force of skilled labour.

It may not be without interest to trace briefly the development of the zinc industry in each of the different centres of production. This will conduce to a more thorough appreciation of the relative positions of the individual localities in contributing to the world's supply of zinc.

### The Development of the British Zinc Industry

As the enterprise at Bristol that marked the beginning of zinc production, not only in Great Britain, but also in Europe, was unsupported by any important domestic deposits of zinc ore, and was handicapped by methods of smelting inferior to those of Belgium and Silesia, it gradually languished and eventually died out about 1860.

Meanwhile, the well-known firm of Vivians had, in 1835, erected zinc smelting works at Swansea in South Wales, around which, as a nucleus, gradually grew the British zinc smelting industry.

<sup>1</sup> H. L. Sulman, Presidential Address. Transactions of the Institute of Mining and Metallurgy, 1910-1911, vol. xx.

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As already indicated, the process of extracting the metal first practised in this country differed very materially from that adopted later in Belgium and Silesia. In the English method of distillation *per descensum*, the zinc vapour was drawn downwards from the bottom of the pot or crucible to the condensing apparatus, whilst in the process *per ascensum* as practised on the Continent the vapour of the metal passed from the uppermost point of the retort or muffle to the condensing apparatus. The English method was conducted in large crucibles heated in a furnace in many respects similar to those used in glass works for the fusion and preparation of glass. The method is said to have entailed only a comparatively small expenditure of manual labour, but it involved a much larger consumption of fuel than in either the Belgian or the Silesian process, and on that account the English process was superseded by the Continental methods of smelting about 1850.

The extensive zinc smelting works erected near Swansea by Mr. Hussey Vivian in 1835 are stated to have contained English, Silesian and Belgian zinc furnaces, from which it would appear that British zinc metallurgists were giving attention to the Continental methods of zinc production some years before they finally abandoned the English method in favour of the Belgian and Silesian processes.

Percy states that in 1861 both the Silesian and Belgian methods of distillation were in use at a large zinc smelting works in this country producing about 100 tons of zinc weekly.

With the growth of the zinc industry, works for the production of the metal were established at Llanelly, Wigan, Wrexham, Sheffield, Birmingham and Bristol, but Swansea has always been the principal centre of zinc production in Great Britain and is still responsible for a large proportion of the metal annually produced in this country.

The early statistics of zinc output in Great Britain are not very trustworthy, but it would appear that prior to 1880 the annual production was under 10,000 tons (English, 2,240 lb.). Four years later the output was 30,000 tons, showing that the production of the metal had increased threefold, due to the progress of the galvanising industry.

Between 1884 and 1887 the output fell to 20,000 tons, and then rose again rapidly to about 31,000 tons in 1889. With the exception of a fall to 24,000 tons in 1896, the annual production averaged about 30,000 tons between the years 1889 and 1901, from which date the output rapidly increased until it reached approximately 50,000 tons in 1905. Since that time the British production of zinc has fluctuated between 50,000 and 60,000 English tons annually.

The accompanying curve shows the approximate annual output of zinc in Great Britain from 1875 to 1915 in metric tons.

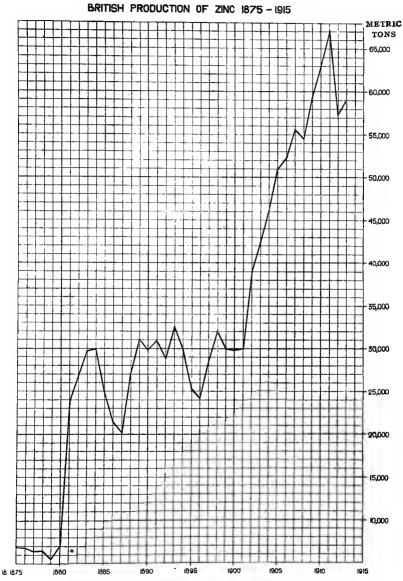
The growth of the British zinc industry is largely due to the rapid progress in the manufacture of galvanised or zinc covered sheets, which soon became an important branch of British metallurgical industry, and created a demand for zinc which became so considerable that the smelters in this country could not keep pace with its constantly increasing requirements. This presented the opportunity for the importation of foreign zinc, an opportunity of which Continental smelters readily availed themselves, with the result that very considerable quantities of metal have for some years been shipped to this country annually, chiefly from Belgium and Germany, a condition of things that must have been very helpful to the development of the zinc industry in those countries. The extent of this importation of foreign zinc to meet British demands may be realised when it is stated that] for some years prior to the war the imports of crude zinc into the United Kingdom averaged about 100,000 tons annually.

The bulk of the imported metal, as shown by the table on p. 26, came from Germany and Belgium, whilst other countries also contributed smaller amounts. It will be seen that the cost of this imported metal amounted to the enormous sum of  $\pounds 3,500,000$  annually, a fact which shows how important an adequate supply of the metal is to British industries, even under normal conditions.

In addition, however, to the imports of crude zinc, about 20,000 tons of manufactured zinc, largely sheet metal, and valued at about  $\pounds$ 600,000, was imported annually into the United Kingdom in the few years immediately preceding the war.

It will be seen that in 1913 the zinc imports amounted to as much as 145,000 tons, whilst the zinc produced in the country in 1913 totalled only 58,298 tons, representing 5.9 per cent. of the world's production of zinc for that year, which was

# THE RISE AND PROGRESS OF THE PRODUCTION



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985,142 tons. It must, however, be pointed out that of the total metal produced in Great Britain in 1913 probably not more than 31,290 tons were "primary" zinc in the sense of being extracted from ores, the balance of 27,008 tons being the result of treatment of by-products, galvanisers ashes, hard-zinc, etc.<sup>1</sup>

It will be seen, therefore, that this country in the year before the outbreak of war was producing—even including "secondary" metal—only about 26.0 per cent. of its zinc requirements.

For many years the galvanising industry has been by far the largest consumer of zinc in this country, probably requiring at the present time nearly 70 per cent. of the total zinc consumed in Great Britain.

With this very important field of zinc consumption so close at hand, it is difficult to explain why British zinc smelters have made so little progress and have allowed the output of metal to fall so far short of the demand that prior to the war fully two-thirds of the British zinc requirements were imported from the Continent and to a small extent from America.

There is doubtless some justification for the assertion that. as the ores of zinc which are to be found within the limits of the British Isles do not equal in importance those of some of the foreign zinc producing countries, the home production of the metal has had to struggle against the superior advantages of some of the foreign sources of supply. But, as pointed out by J. Gilbert,<sup>2</sup> more than one half of the zinc imports to the United Kingdom have hitherto come from Belgium and the Rhine district, where for some years fully 33 per cent. of the European production of zinc has been produced almost exclusively from ore imported from all parts of the world; consequently the above assertion loses much of its weight. One must therefore look for other causes in order to explain the apparent neglect of the zinc industry in Great Britain, and the principal one will be found in the fact that the British smelters have scarcely availed themselves to any great extent of the enormous progress made by the Continental smelters in the improvement of their furnaces, whereby they have been enabled to reduce the former considerable loss in smelting by from 33 to 50 per cent. This source of economy became of special importance when the old supplies of the rich and comparatively easily smelted carbonate of zinc (calamine)

<sup>1</sup> Rudolf Wolff & Co., published statistics for 1913.

<sup>2</sup> The Mining Journal, 1916, vol. cxiv, p. 480.

were gradually diminishing, and the treatment of the originally neglected sulphide of zinc (blende) had to be resorted to. The experiments in that direction, started in Germany and

The experiments in that direction, started in Germany and Belgium some twenty years ago, have gradually led to such important improvements in the old type of furnaces, chiefly in reducing the ruinous loss in smelting and in the saving of fuel, retorts, and labour, that these factors may be considered as the principal sources of prosperity of the Continental "Lohnhuetten" ("customs") works, that purchase ores for treatment, in contradistinction to "Grubenhuetten" works, which treat ores produced by their own mines. Most of the "Lohnhuetten" companies, during the last ten to twenty years, have equipped their works with modern furnaces.

As J. Gilbert remarks, "Unfortunately, the British zinc smelters and consumers have not watched the rapid development of the industry on the Continent, which went hand in hand with some enormous contracts for ore, chiefly from mines situated in the British Colonies, with sufficient alertness to enable them to participate in the financial results realised during the last decades, to such an extent as their position as principal consumers of zinc in Europe might entitle them.

"The smaller British zinc companies shrank from the responsibility which the outlay for the comparatively expensive modern plant would involve, and the larger companies most likely had sufficiently profitable employment for their capital and labour in other metallurgical enterprises, that the prospects of zinc might have appeared to them as a *quantité négligeable*. Thus, generally speaking, very little progress has been made by British zinc makers during the last thirty to forty years, which fact is also shown by a comparison of the values of British zinc shares with, for instance, Belgian shares."

Although economic reasons have had something to do with the lack of enterprise in the British zinc industry, it would appear that a certain amount of conservatism, and perhaps an undue regard for local tradition on the part of the zinc metallurgists and the natural desire of our financiers to see a fair return on their capital, such as they have hitherto more readily obtained elsewhere, are mainly responsible.

Two important circumstances which also appear to have retarded the development of the British zinc smelting industry are lack of scientific control and want of co-operation between the different smelting companies, in which respects the British industry compares unfavourably with that of the Continent.

The increasing cost of production during the past few years has emphasised the necessity for scientific control.

Whilst there are instances where individual firms keep themselves informed regarding scientific developments in zinc metallurgy and make efforts to improve working methods, there is little doubt that a fuller appreciation of the value of the scientifically trained metallurgist and of co-operative action is needed in order to produce general increased efficiency. This statement should not, however, lead to the erroneous conclusion which some persons are inclined to draw, that British metallurgists are too ignorant of chemical knowledge to understand the theory of the processes under their direction. It is not too much to affirm that with respect to knowledge, both of the theory and practice of the special departments of the art in which they are engaged, the zinc smelters of this country are in many cases not excelled by any metallurgists in Europe. But while progress, although slow, has been made in the past, much more will have to be done in the future, since the unprecedented times through which we are now passing demand a long step forward in knowledge, equipment, and organisation. The advantages of co-operation are too self-evident to need emphasising here.

As has been well said,<sup>1</sup> "the spirit of co-operation is not a mere sentiment or theory. It has been as much a scientific necessity for the winning of this war as the provision of guns and ammunition, and it will be equally a scientific necessity to success in the arts of peace." Co-operation will be secured as the result of confidence between individual firms engaged in the same industry and between employer and employed. The value of co-operation has long been recognised by the zinc smelters on the Continent. Some years ago a society was started in Germany in the interests of the producers of non-ferrous metals, and sections were formed to deal with special branches of industry, including a zinc section consisting of the managers and higher technical officials of the zinc smelting works.<sup>2</sup> They met at the same time as the half-yearly meetings of the society, and

<sup>&</sup>lt;sup>1</sup> Prof. W. Ripper, "Works Organisation and Efficiency," Journal of Royal Society of Arts, 1917, vol. lxv, p. 461.

<sup>&</sup>lt;sup>a</sup> H. M. Ridge, Journal of the Society of Chemical Industry, 1915, vol. xxxiv, p. 764.

exchanged experiences confidentially. No reports of the sectional meetings were published, since they were only for the mutual benefit of the members and for the promotion of German industry, but the system has given excellent results. Some such system might with advantage be adopted in this country. The first step would be to consider the means needed to overcome the hindrances which have occasioned the lack of co-operation in the past.

Probably an amalgamation of various zinc smelting works would be the easiest means of attaining the desired end.

It is necessary to realise that the industry must move forward as a whole if the greatest advantage is to be gained, and this can only occur by the loyal co-operation of those engaged in it and by the cultivation of a spirit of confidence in each other.

It is much to be regretted that the schemes so far suggested will not increase the British output of zinc sufficiently to relieve entirely consumers of their dependence on foreign supplies.

The proposals that have been made for the development of the zinc industry are dealt with in Chapter XIII (p. 198).

Speaking generally, it may be said that the British zinc industry has always been dependent on imported ores. Almost as soon as the industry became firmly established important zinc mines in Sardinia were operated by British zinc smelting companies, the ore being shipped to Swansea for treatment. As early even as 1870 the small production of zinc ore in Great Britain was decreasing, the output for that year amounting to only 18,500 tons, equivalent to approximately 5,000 tons of metallic zinc, whilst a considerable tonnage of zinc ore was exported from Sardinia to Swansea in that year. From that time forward the British smelters have imported increasing quantities of zinc ore annually.

For many years the zinc mines in the United Kingdom have yielded only an average output of some 17,000 tons, the bulk of which was mined by the Vieille Montagne Zinc Company of Belgium, and exported to that country for treatment. The small quantity of British ores smelted in this country produce about 2,500 tons of zinc annually, the remainder of the metal produced in the United Kingdom being obtained from imported ores as already stated.

4	From			JI	1012.	IC	1013.	-	TOTA
									.+
				Tons.	77	Tons.	72	Tons.	4
Germany	:	:	:	54,686	I,429,655	64,179	1,503,023	33,49I	730,441
Belgium	:	:	:	57,207	I,495,850	53,500	1,291,011	27,312	615,538
Netherlands	:	:	:	9,992	264,572	13,301	320,091	12,189	284,691
France	:	:	:	5,983	150,879	5,915	144,921	3,183	69,876
United States	:	:	:	4,915	129,223	4,670	116,292	35,068	939,199
Canada	:	:	:	266	19,712	962	18,514	1,319	25,526
Other Countries	:	:	:	3,488	84,239	2,477	56,826	3,297	84,536
Ţ	Total	:	:	137,268	3,574,130	145,004	3,450,678	115,859	2,749,807
	П	MPORTS	S OF 2	ZINC ORE INT	IMPORTS OF ZINC ORE INTO THE UNITED KINGDOM. <sup>1</sup>		(ENGLISH TONS, 2,240 LB.)	0,240 LB.)	
Ð	From			51	1912.	5 <b>1</b>	1913.	5I	1914.
				Tons.	F.	Tons.	7	Tons.	7
Australia	:	:	:	20,611	113,500	16,772	83,892	78.503	411.586
Italy	:	:	:	13,963	121,191	13,801	I06,826	23,280	I 52,706
geria	:	:	:	8,707	62,429	9,302	61,82I	6 <b>,9</b> 29	35,662
ann	:	:	:	8,417	44,512	6,348	27,162	6,474	29,295
Germany	:	:	:	5,004	47,742	7,169	58,227	5,190	39,938
France	:	:	:	3,408	31,779	4,337	28,875	3,175	20,362
Kussia	:	:	:	21	270	315	I,443	6,436	36,737
Japan	:	:	:	1	1	1,190	I0,020	5,191	44,380
her Countries	:	:	:	7,208	60,206	5,436	39,362	9,073	46,337
To	Total	:	:	62,339	481,629	64,670	417,628	144,251	817,003
			-	-			1	1	*

THE ZINC INDUSTRY

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The quantity and the sources of zinc ore imported into the United Kingdom for the three years 1912 to 1914 are shown in the table on p. 26.

There are almost unlimited supplies of high grade zinc ore within the British Empire that have long been available for zinc smelters, but it is only within quite recent years that any quantity of the ore has found its way to this country for the extraction of the metal.

It will be seen from the table on p. 26 that in 1914 there was a very large increase in the quantity of ore imported from Australia. Prior to the war a very considerable proportion of the Australian output of zinc ore was controlled by German firms and shipped to the Continent for smelting. Further reference to this question will be found on p. 152.

It is very regrettable that so much of the work done by Englishmen in devising means of dressing the vast supplies of zinc-lead ores of Broken Hill, Australia, should have merely resulted in our becoming suppliers to the Continental smelter firms who readily treated such ores, because our smelters were not prepared to pay a price which would induce the sellers to send them to this country, or to adapt their furnaces for their special treatment.

There are now seventeen works producing zinc and remelting scrap zinc, etc., in Great Britain, seven being situated in the Swansea Valley, the chief centre of production, and the remainder in different parts of the country.

In the selection of a locality for the erection of zinc works, it is requisite not only that the ore should be delivered at a reasonable price, but also that good coal and very superior fireclay should be readily obtainable. These conditions are well met in Swansea, and on that account this district was early selected as the chief seat of the British industry.

About ten works produce zinc direct from ores to the extent of approximately 31,000 tons, while the remaining seven works produce "secondary" zinc amounting to approximately 27,000 tons, thus making the total output 58,000 tons for 1913. The bulk of the secondary zinc is extracted from the by-products of the galvanising works, and the zinc works for the treatment of this material are therefore usually situated near the centres of the galvanising industry.

#### THE ZINC INDUSTRY

The actual position of the works producing zinc in the United Kingdom is shown in the following list:---

LIST OF ZINC SMELTERS AND ZINC EXTRACTORS IN THE UNITED KINGDOM.

Count	y.		Owner of Works.	Situation of Works.
Cheshire	••	••	Brunner, Mond & Co., Ltd.	Northwich.
Durham	••	••	Central Zinc Co., Ltd.	Seaton Carew.
Glamorganshire	÷	••	British Metals Extrac- tion Co., Ltd. (Villiers Smelting Works).	Llansamlet.
,,	••		Dillwyn & Co., Ltd.	Llansamlet.
,,	••		Down & Co., Ltd.	Swansea.
,,	••	••	English Crown Spelter Co., Ltd.	Swansea (Port Ten- nant).
,,	••	••	Williams, Foster & Co., and Pascoe, Grenfell & Sons, Ltd. (Upper Bank Spelter Works)	Swansea.
,,	••	••	Swansea Vale Spelter Co., Ltd.	Llansamlet.
,,	••	••	Vivian & Sons (Morris- ton Spelter Works).	Swansea.
Lancashire	••	••	New Delaville Spelter Co., Ltd.	Warrington.
			The British Electro- lytic Zinc Co.	Widnes.
Middlesex	••	••	Thos. W. Ward, Ltd.	Silvertown, London, E.
Somersetshire	••	•••	John Lysaght, Ltd. New Delaville Spelter Co., Ltd.	Bristol. Bloxwich.
Warwickshire	••	••	New Delaville Spelter Co., Ltd.	Birmingham.
Worcestershire		••	Stewarts & Lloyds, Ltd. (Coombs Wood Tube Works).	Halesowen, near Bir- mingham.
Ayrshire	••	••	Brands Pure Spelter Co., Ltd.	Irvine (Glasgow).

Previous to the war the Swansea Vale works belonged to an influential German firm, who had installed a modern smelting plant capable of producing 10,000 tons of spelter per annum. Practically all the shares in the company are now held by the Share Guarantee Trust, Limited, and the works, which are now the largest in Swansea, are being further enlarged.

The works at Seaton Carew, Durham, which are modern and well equipped, are operated by the Sulphide Corporation, and before the outbreak of war were treating annually some 10,000 to 12,000 tons of zinc concentrates from the Broken Hill mines ; since the war the works have been enlarged, and a considerable increase in output of zinc from these ores will result in future.

Formerly the whole of the zinc produced in Great Britain was extracted by distillation, but within recent years the deposition of zinc from solution by electrolysis has been introduced by Messrs. Brunner, Mond & Co., Ltd., Northwich, and zinc of very high grade is now being produced by this method. Since the beginning of the war Messrs. Chance and Hunt, of Oldbury, and the British Electrolytic Zinc Company, of Widnes, have also commenced the production of electrolytic zinc, for which there is an increasing demand on account of its freedom from impurities.

### British Empire Centres of Zinc Production

In addition to the old-established zinc smelting centre of Swansea, various plants have been erected in modern times to deal more particularly with zinc ores occurring within the British Empire.

Many of these ores are of a complex nature, and in connection with their treatment there has been a very important development in the field of electrolytic methods of zinc extraction.

Australia.—Foremost amongst the newer smelting plants are those erected at Port Pirie and at Cockle Creek, near Newcastle, New South Wales, to smelt the lead ore product from the vast deposits of complex lead-zinc sulphides mined at Broken Hill. The nature of these ores is dealt with later (see p. 53).

The satisfactory treatment of these ores for the recovery of both lead and zinc has presented considerable difficulties to the metallurgist, and it is only within quite recent years that the profitable extraction of zinc has been rendered possible. The modern methods of dressing the ore yield two products, one of which is rich in lead and is smelted for that metal, and the other rich in zinc, which is smelted for its zinc content.

The Port Pirie smeltery takes the lead concentrate and the zinc concentrate from the Broken Hill Proprietary, Zinc Corporation, Junction, Junction North and Amalgamated Zinc Companies. The Sulphide Corporation smelts its lead ore at Cockle Creek, together with the lead ore from Block 14 Mine. In the earlier working of the Broken Hill deposits for lead and silver, the zinc was neglected and enormous quantities of zinciferous tailings and slimes accumulated from the concentrating plants.

In addition to these, some of the slags from the lead smelting contained from 16 to 20 per cent. of zinc oxide. It was estimated by the New South Wales Department of Mines that in 1903 there had accumulated zinc residues and tailings amounting to 5,687,400 tons, and these contained 18.6 per cent. of zinc. Numerous processes were tried in order to produce a marketable grade of ore from these residues, and it was finally decided that flotation processes were the most suitable.

The importance of these residues at the present time is well illustrated by reference to the operations of only one company, the Amalgamated Zinc Company, which in 1913 treated 498,289 tons of tailings which contained zinc,  $17\cdot1$  per cent.; lead,  $3\cdot7$ per cent., and silver,  $4\cdot4$  oz. per ton.<sup>1</sup>

From these residues there were obtained 140,098 tons of zinc concentrates carrying zinc, 48.9 per cent.; lead, 5.9 per cent., and silver, 8.5 oz. per ton. The lead concentrates also produced amounted to 1,584 tons and contained lead, 57.1 per cent.; zinc, 15 per cent., and silver 35.2 oz. per ton. The lead and zinc concentrates together were valued at  $\pounds$ 392,182. In 1913, the total value of the products obtained by the companies engaged in treating zinc-bearing tailings was  $\pounds$ 776,228. Most of the "dumps," or reserves of tailings, have now been treated.

The annual output of crude ore from the Broken Hill district amounts to about 1,700,000 tons, and employment is found for about 8,800 men. These figures give some idea of the great importance of the deposits as a potential source of lead, zinc and silver.

The annual output of zinc concentrate in normal times is approximately 500,000 tons, valued at about £1,500,000. Prior to the war, about 41.5 per cent. of the lead concentrates produced at Broken Hill was smelted at Port Pirie, and 8.5 per cent. at Cockle Creek, while the remaining 50 per cent. was dispatched to Belgium, Germany, France and Austria, where it was handled almost entirely by German firms. Of the zinc concentrates, only about 2.5 per cent. was smelted annually at Port Pirie, and with the exception of some 20,000 tons which is exported

<sup>1</sup> Bulletin of the Imperial Institute, 1915, vol. xiii, p. 621.

to the United Kingdom and smelted at the works of the Sulphide Corporation at Seaton Carew and other works, the bulk of the remainder was dispatched to smelters in Belgium and Germany under long term contracts.

The disposal of the lead concentrates was on very different lines, at least one half of the ore being smelted locally, as stated above, and the remainder sold under short-date contracts, chiefly to German firms.

The output of zinc from the Australian smelting plant has, up to the present, been too small to have any effect on the world's production, owing to the large amount of zinc concentrate shipped before the war to Europe, but which, in view of the proposal to enlarge the Port Pirie smelting plant, may become more important in the near future. This extension forms part of the scheme that has been proposed since the outbreak of war with a view to increase the output of zinc within the British Empire.

Tasmania.—Some experimental plants are in course of erection in Tasmania for the treatment of the complex zinc-bearing ores of the Mount Read district by electrolytic methods. Reference to the processes to be used will be found on p. 134.

This enterprise, which has been discussed for some ten years, embraces, not only a large plant which is being erected by the Australian Electrolytic Zinc Company, with a suggested capacity of 45,000 tons of zinc per annum, and Gillie's works at Hobart, but all the fresh range of output from the Tasmanian West Coast ores.

Canada.—Although zinc ores have been mined in Canada for some years, it is only quite recently that attempts have been made to treat them in the country. Formerly the ore was shipped to the United States for treatment, but since the outbreak of war considerable attention has been given to the question of treating the ore in Canada.

To encourage the erection of zinc extraction plants, the Canadian Government recently agreed to grant bounties on a sliding scale, not exceeding 2 cents (1*d*.) per lb., on the production of zinc in Canada from Canadian ores when the standard price of zinc in London (England) falls below £33 per ton of 2,000 lb. Such zinc must not contain more than 2 per cent. of impurities.

There are deposits of low grade and leady zinc ores in Canada that can only with difficulty be concentrated so as to produce high grade lead and zinc concentrate respectively.

In the past there has been a moderate production of zinc concentrates for export to American smelters, the treatment charges and high freight rates serving to prevent any very extensive development in this direction. Some 7,000 to 9,000 tons of zinc ores and concentrates, containing about 3,000 to 4,000 tons of zinc, have been shipped annually in recent years. At the beginning of the war the smelters in the United States declined to take further shipments of zinc ores from British Columbia, and there was at that time in Canada a shortage of zinc for use in manufacturing ammunition and a quantity of zinc ore that could not be disposed of. A Commission was appointed by the Minister of Militia and Defence to look into the matter on behalf of the Government.<sup>1</sup> It was found to be impossible to obtain the pure zinc for use in the manufacture of cartridge brass from the British Columbia ores by any distillation process, whether in the Belgian retort or in the electric furnace. It was therefore necessary to turn to hydro-metallurgy, and after a large amount of experimental work a process has been developed at the works of the Consolidated Mining and Smelting Company at Trail, B.C., and at some other smelters, which is a modification of the well-known Létrange process, the ore being roasted, leached with sulphuric acid, and the resulting zinc sulphate solution electrolysed with insoluble anodes. During 1916 a large plant was built at Trail, costing perhaps 1,000,000 dollars, and capable of producing 30 or 40 tons of electrolytic zinc per day, which should meet in large measure the present requirements for cartridge brass in Canada.

Similar work is going on at Welland in Ontario, at a large plant owned by the Weedon Mining Company. Prof. Stansfield, of McGill University, considers that "this development was undoubtedly the best under the existing circumstances, but it must not be supposed that it disposes of the possibility of smelting these ores in the electric furnace." The works at Welland will be supplied with ore from the mines owned by the company at Welland and at Nottingham, Quebec.

According to a recently issued report of the Canadian Department of Mines, Ottawa, the shipments of zinc ores to America in 1915 amounted to 14,895 tons, valued at 554,938 dollars, and containing 12,231,439 lb. of zinc.

<sup>1</sup> A. Stansfield, Journal of the Institute of Metals, 1916, No. 1, vol. xv, p. 292.

Assuming a probable recovery of 80 per cent. of the metal, the production of zinc in 1915 from Canadian ores may be put at 9.785.151 lb. (approximately 5.000 short tons), valued at 1.294.575 dollars. Adding to the result of a similar estimate for 1916 the actual output of zinc at Trail, it would appear that the production of zinc from Canadian ores in that year was 23.515.030lb. (approximately 12.000 short tons), valued at 3.010.864 dollars. According to the Report for 1916 of the British Columbian Minister of Mines, the output of zinc from the smelter at Trail in that year was approximately 15,000,000 lb. (7,500 short tons). At the beginning of 1917 the output of the smelter was stated to be from 25 to 30 tons per day.

# The Development of the European Zinc Industry

The position taken by Europe as the largest contributor to the world's supply of zinc has been maintained until the present time. In 1913 Europe's share of the world's output of zinc was 673,900 metric tons, or 675 per cent. of the world's total output for that year.

The bulk of the metal was produced in Germany and Belgium. Thus, in 1913, Germany's output was nearly 42 per cent. of Europe's production and about 28.4 per cent. of the world's total for that year, whilst Belgium contributed about 40 per cent. of the European production.

The zinc production of the remaining European countries is much smaller than that of Germany and Belgium.

The British output hardly exceeds 10 to 12 per cent. of the European production, whilst British consumers of zinc absorb about 40 per cent. of the European output.

Next in importance as producers in Europe are France, Holland, Austria-Hungary, Norway and Sweden.

Compared with the old-established British, German and Belgian industries, zinc production in the other European countries must be regarded as of comparatively modern origin.

As the result of the ever-increasing demand for zinc, the European zinc industry made rapid progress, notably in Germany and Belgium, during the latter part of the nineteenth century.

Germany.—Taking advantage of her extensive natural resources in zinc ore and coal, Germany early took the lead as the largest producer not only in Europe, but in the world, a lead which she maintained for many years; but in recent years the first place in the world's zinc producers has been taken by America.

The growth of the zinc industry in the German Empire is shown by the following figures :—In 1862 the output was about 55,000 metric tons; in 1872 it amounted to 58,400 tons; ten years later the output had nearly doubled, the total for 1882 being about 106,000 tons, while in 1892 it had reached a total of approximately 140,000 tons, thus showing an increase of about 139 per cent. in twenty years, equivalent to an advance of about 8 per cent. per annum since 1885.

A further ten years saw a considerable augmentation of output, the total for 1902 being about 190,000 tons, which had increased to approximately 271,000 tons in 1912.

The production for 1913 was 283,113 tons, showing an enormous increase on the output of ten years previously.

The chief zinc producing centre of Germany is Silesia, the output from this district being about two-thirds of the total production of the German Empire, the remainder coming chiefly from the Rhine district and Westphalia.

The actual production of zinc, in metric tons, from these two districts in recent years is shown in the following table <sup>1</sup>:---

District.		1909.	1910.	1911.	1912.	1913.
Silesia Rhine District Westphalia	and	<b>139,</b> 690 75,173	140,249 78,765	156,174 81,458	169,088 86,619	170,119 92,852

PRODUCTION OF GERMAN ZINC IN METRIC TONS (2,204.6 LB.)

The Silesian zinc industry is confined to the extreme southeastern part of Prussia, in a somewhat narrow strip of territory between Russia and the Austrian frontier.

Established, as already stated, in the latter part of the eighteenth century, it was prior to the war an industry of considerable magnitude, taking a very prominent part in supplying the European markets with zinc.

Formerly the metal was produced entirely from domestic

<sup>1</sup> Compiled by Henry R. Merton & Co., London.

ores, but in more recent years considerable amounts of ore have been imported.

For some years Germany has adopted the policy of conserving national resources for the future, and of buying ore in foreign markets when this could be done on terms which would permit of a good profit on the smelting.

It has been stated recently<sup>1</sup> that several of the mines in Silesia, particularly those of Hohenlohe and Giesche, have milling and concentrating plants which are only being worked to something between 30 and 40 per cent. of their possible capacity. The Von Giesches Erben is reported to possess ore reserves which at the rate of mining in 1914 are estimated to last for more than 100 years.

From the reports which have reached this country since the war commenced, it would appear that Germany has suffered no shortage of zinc, her domestic ores and established smelting industries having supplied all demands and enabled the metal to be sold at very little above the pre-war average price.

The zinc smelting industry of Upper Silesia is in the hands of several large firms, the metallurgists of which stand at the head of their profession and have brought the industry to a high state of perfection.

The works are divided into two main classes—(1) the "Grubenhuetten" or "Erzhuetten" companies, which smelt ore produced by their own mines, and (2) the "Lohnhuetten" companies, which buy ore in the market.

These latter have yielded good profits in recent years, being supported by the leading wealthy metal and mineral trading companies, who have large interests in the zinc industry. Nothing has been spared to develop the dominant position taken by the German zinc industry, and during the past ten years most of the works have been reconstructed and supplied with modern gas-fired furnaces, and many improvements have been introduced into both the roasting and smelting processes.

Although the number of smelting concerns engaged in the zinc industry in 1870 was 35, the number had been reduced to 29 in 1890, but the capacity of these works was increased so that the output of metal was augmented. Since 1890, a few new works have been added to enable the output to be brought to the large figure which represents the modern production.

1 H. M. Ridge, Journal of the Institute of Metals, 1916, vol. xvi, p. 187.

#### THE ZINC INDUSTRY

The German output of zinc, in metric tons, for the ten years ending 1913 is as follows :----

Year.	Metric tons.	Year.	Metric tons.
1904	191,060	1909	220,080
1905	197,184	1910	227,747
1906	205,023	1911	250,393
1907	208,707	1912	271,064
1908	216,876	1913	283,113

GERMAN OUTPUT OF ZINC.

Since the production has for many years been in excess of the consumption of zinc in Germany, the surplus metal has been exported, chiefly to the United Kingdom.

The smelting of sulphide zinc ores in Germany led to the establishment of very complete arrangements for utilising the sulphurous acid generated in the roasting of the ore, the first practical results in this direction being obtained by Hasenclever as early as 1855.

Most of the works are now equipped with special roasting furnaces, which permit of the roast gases being used for the manufacture of sulphuric acid, and there is little doubt that the utilisation of the sulphur in zinc ores for this purpose has contributed very materially to the success of the Continental zinc smelting industry.

Sulphuric acid is a by-product of considerable commercial value, and consequently a source of additional profit to zinc production. The question of roasting blende for sulphuric acid production is more fully discussed when dealing with the by-products from zinc smelting on p. 111.

In addition to the production of zinc and sulphuric acid, the Silesian industry includes a number of zinc-rolling mills which contribute a considerable quantity of sheet metal to the world's requirements. Prior to the war, eight mills were producing about 50,000 tons of sheet metal per annum.

Austria-Hungary.—The zinc production from these countries is comparatively small, although the output has gradually increased in recent years. The output rose from 19,600 metric tons in 1912 to 21,700 tons in 1913. The larger proportion of the metal is produced at the works in Galicia, whilst rather less than 50 per cent. is obtained at the works at Steiermark.

Belgium.—As already stated, Belgium early became the second largest zinc producer in Europe, producing about two-thirds of the European output in 1890, but so rapid has been the increase in later years that prior to the war the output almost equalled that of Germany.

The Belgian zinc production in recent years is shown in metric tons in the following table :---

Year.	Metric tons.	Year.	Metric tons.
1904	139,982	1909	167,100
1905	145,592	1910	172,578
1906	152,461	1911	195,092
1907	154,492	1912	200,198
1908	165,019	1913	197,703

BELGIAN OUTPUT OF ZINC.

Zinc rolling also forms an important branch of the industry, the production of sheet metal in 1913 being 51,500 metric tons, as against 49,100 tons in 1912.

A small proportion of the output of crude zinc is utilised for the production of zinc oxide (zinc white) by burning the metal in air as described later (p. 192).

The Belgian industry was founded to utilise the important deposits of ore in the country, but since 1856 the yield of native zinc ore has been comparatively small, so that it has been necessary to import increasing quantities of foreign ores to maintain the large production of metal in modern times. Within recent years considerable quantities of zinc concentrates from Broken Hill, Australia, have been smelted in the country. The Belgian zinc smelting works are situated in the neighbourhood of Liége and are owned by the well-known Vieille Montagne Spelter Company, but are largely under German control.

The company has works, or mines, not only in Belgium, but also in France, Germany, Sweden, England, Algeria and Italy.

Much that has been said regarding the German zinc smelting works applies equally to those in Belgium.

The works are well equipped with modern plant, including gas-fired furnaces and roasting furnaces which permit of the utilisation of the sulphur gases for the production of sulphuric acid. Prior to the war there was a considerable surplus in the production of this commodity in Belgium in consequence of the enormous quantities of zinc blende roasted in that country.

The future of the Belgian zinc industry is very uncertain, as there is some doubt as to the fate of the works when the enemy are obliged to evacuate the country.

It is reported that the Germans are keeping together the skilled labour of the Belgian zinc works, and that they are assisting in the running of some of the works, but since the available supplies of ore are limited it is doubtful whether the vield can be very large.

The German control of the Belgian zinc industry is not likely to continue after the war.

France.—The production of zinc in France is very little in excess of that required for home consumption. Although a moderate producer of zinc ore, much of the ore smelted is of foreign origin. The smelting works are situated at Pontgiband, and in recent years the metal produced has been of high grade. In 1912 France contributed 64,300 metric tons of zinc to Europe's supply, and 61,100 tons in 1913, thus showing a small decrease. In each of these years about 5,000 tons were exported to the United Kingdom.

The consumption of zinc in France amounted to 82,000 tons in 1912, and 81,000 tons in 1913, thus showing a falling off.

Holland.—Zinc production in Holland has shown a steady increase in recent years, the production for the ten years ending 1913 being as follows :—

Year.	Metric tons.	Year.	Metric tons.
1904	13,099	1909	19,548
1905	13,767	1910	20,975
1906	14,650	1911	22,733
1907	14,990	1912	23,932
1908	17,257	1913	24,323

PRODUCTION OF ZINC IN HOLLAND.

Spain.—Only a small proportion of the zinc ore raised in Spain is smelted in the country, the bulk being treated in France and other centres of production.

The leading Spanish zinc works are those of Penarroya in Cordoba and Arnao in Oviedo. The output amounted to 8,000 metric tons in 1912 and 10,000 tons in 1913. In April, 1915, the export of zinc in cakes was embargoed, and on January I, 1916, an export tax equal to 37s. 6d. was placed on zinc in pigs, blocks and waste articles, and the import duty was removed.

Norway.—Within recent years Norway has become a small producer of zinc, the output in 1911 being 6,680 metric tons, that of 1912, 8,128 tons, and 9,287 tons in 1913.

Sweden.—A special feature of zinc production in Sweden is the application of electric smelting processes to which reference is made later (p. 124). The development of these processes has been rendered possible by the plentiful supply of water power in the country, which has been utilised for generating the necessary electrical power.

Sweden produced, in 1913, 6,900 tons of ordinary zinc and 2,000 tons of fine zinc.

*Russia.*—Up to the present the production of zinc in Russia has been small, the zinc smelting industry being of comparatively recent introduction. There are good deposits of zinc ore in the country, more especially in Poland, the chief sources of the ore smelted being the mines at Ulisses and Boleslaw, near Olkusch. Prior to the war the annual output of zinc in Russia was between 8,000 and 9,000 metric tons, whilst the average consumption was more than three times this amount.

The production, in metric tons, for the ten years ending 1913 was as follows  $^{1}$ :—

Year.	Metric tons.	Year.	Metric tons.
1904	10,606	1909	7,945
1905	7,642	1910	8,631
1906	9,610	1911	9,936
1907	9,738	1912	8,763
1908	8,839	1913	7,610

PRODUCTION OF ZINC IN RUSSIA.

Owing to heavy requirements in roofing sheets, Russia consumed 33,300 tons of zinc in 1913, as compared with approximately 28,000 tons in 1912. On the other hand Russia's

<sup>1</sup> Compiled by Henry R. Merton & Co.

production declined in 1913 to the extent of 1,200 tons, as shown, which was made up for by the increase of 6,600 tons in her imports of zinc in cakes and sheet metal. To meet home requirements Russia has hitherto been obliged to import over 20,000 tons of zinc annually, most of which was obtained from Germany.

It would appear that attempts are now being made to develop the Russian zinc smelting, as, according to the United States of America Consular Report for 1916, a large zinc smelting works is being erected at Hikoshuna, in the Shimonoseki Straits, by the Su uki Shoten of Kobe. It is proposed to treat at these works ore derived chiefly from Asiatic Russia and Australia.

### The Development of the American Zinc Industry

Although started more than half a century later than that of Europe, the American zinc industry has made such rapid progress, especially during the past few decades, that the United States have since 1906 held the premier position as a producer of zinc.

In 1913 the United States contributed 32'1 per cent. of the world's supply of zinc, whereas Germany, formerly the largest producer, contributed 28'4 per cent.

This rapid growth of zinc production in the United States has been rendered possible by the possession of very large quantities of raw material in the form of zinc ore, and of coal, and more particularly of large supplies of natural gas, which, in some localities, is used as the source of heat in smelting the ore, and has proved to be of considerable importance in the economic production of the metal.

The remarkable progress of the American zinc industry affords a striking illustration of the speed with which industrial enterprises develop under the combined influence of great natural resources and of modern smelting plant used with intelligence and skill.

This progress can best be seen by comparing the data of production thirty years ago with those of the present time.

In 1885 the total production of zinc in the United States amounted to only 40,000 metric tons, whilst the production in 1905, twenty years later, had increased five-fold, being more than 200,000 tons. By 1913 the output had increased more than 50 per cent., and since the outbreak of war the production of zinc in America has reached nearly twice the pre-war figure, as shown by the following returns:—

Year.	Metric tons.	Year.	Metric tons.
1907	226,838	1912	314,512
1908	189,941	1913	320,283
1909	240,446	1914	328,731
1910	250,627	1915	446,788
1911	267,472	1916	609,906

ZINC PRODUCTION IN THE UNITED STATES IN METRIC TONS.

With the growth of the industry, zinc smelting works were established in the States of Illinois, Kansas and Missouri, which in pre-war days produced about two-thirds of the total output of American zinc, the remainder being produced in a few Eastern and Southern States.

In consequence of a falling-off in the yield of the natural gas springs of Kansas and Oklahoma in recent years, it became necessary to transfer the works to Illinois and other places where coal or oil could be obtained in sufficient quantity and at a cheap rate. At the end of 1914 there were 33 zinc smelting plants in operation in the United States, their disposition being as follows : Illinois 10, Kansas 9, Oklahoma 6, and the remaining 8 in the States of West Virginia, Missouri, Pennsylvania and Colorado.

The works are independent of each other, so that the competition for ore is keen.

The American zinc industry has always been independent of the European industry, and it is generally agreed that in normal times America is not favourably situated to compete with the European markets, and the shipment of zinc to the United Kingdom only becomes possible when the zinc market is abnormally high, as it has been since the outbreak of war. American smelters have the advantage of being entirely independent of foreign ore, as they have enormous native deposits on which to draw.

The supplies of rich ores from the older districts, such as the famous Joplin district, on which the smelters formerly depended, have been considerably augmented in recent years by concentrates from the complex ores from the Western States. The greatest impetus was given to the production and utilisation of the Western ores by the development of the methods for dressing and separating the complex zinc ores by the aid of electricity, to which reference is made on p. 70.

Previous to the war, the production of zinc in the United States was about equal to the consumption in that country; thus in 1913 they produced 320,283 metric tons of zinc, and consumed 313,300 tons. The balance available for export was therefore only 6,983 tons.

The cutting off of the European supplies of zinc at the outbreak of war resulted in the Allies with one accord turning to the United States, the largest producer of zinc in the world, for supplies, and the response made by the American smelters considerably eased the serious situation in which this country and her Allies found themselves owing to shortage of zinc for munition purposes.

The limited supply of zinc available for export, however, led to a rapid rise in the price of the metal, and the American zinc smelters have been very highly paid for their services.

The deficiency in the world's supply of zinc has been met by the rapid erection of additional works in the United States, and an increase of production has resulted which as the figures given below show, is unprecedented in the history of the zinc industry.

As Professor Carpenter remarks, "What these figures mean can be adequately appreciated only by those who know what is involved in the expansion of an industry where mining and ore-dressing operations, transport and assemblage of materials, erection and operation of furnaces, and, most difficult of all, the training of the necessary labour are concerned."

Taking the individual States in the order of their zinc output, Illinois comes first, then Oklahoma, and Kansas third. As shown by the following figures, these three States are now producing collectively nearly three-fourths of the total output of zinc in the United States.

			·	1915.	<b>1</b> 916.
State.				Metric tons.	Metric tons.
Illinois	••	••		145,105	163,612
Oklahoma	••	••	••	99,073	148,859
Kansas	••	••	••	92,010	127,475
Other States	••	••	••	107,892	157,429
Total	••	••	••	444,080	597,375

Considerable additions are still being made to the smelting plants, so that the future output of zinc will be greater even than that for 1916. The full capacity of the furnaces was not utilised in smelting ore at any time during the past three years; a large number of the retorts were occupied in redistilling crude zinc for the production of high grade metal for munition purposes, much of which was exported to this country.

In 1916 two new smelteries, with large graphite retorts, were erected for this purpose. The high prices of zinc ruling during the past few years have greatly stimulated research in the treatment of low grade complex zinc ores, and America is now producing appreciable quantities of high grade zinc from such ores by electrolytic methods which are described on p. 124.

The enormous increase in zinc production will no doubt make America a formidable competitor of this country after the war. The zinc smelters have been making very large profits, and these have been used wisely in improving the plant, so as to make it as efficient as possible, and in accumulating great financial reserves.

In view of the large ore reserves in America, there is no reason to suppose that there will be any failure to realise the enormous output expected through smelting plant being in excess of the capacity of the mines.

#### Zinc Production in Asia

The Asiatic centres of zinc production, although at present contributing but little to the world's supply, are by no means unimportant, especially in view of recent developments in Japan.

China.—As previously stated, China has for several centuries been a producer of zinc by crude distillation in pots by native methods, and small quantities of metal made in this manner have found their way to the European market for very many years. No details are available as to the amount of metal produced annually, but the amount of metal exported to Europe in recent years is stated to be as follows. In 1911, 710 metric tons; in 1912, 760 tons, and in 1913, 908 tons. The metal, which is produced chiefly at Kweichow, probably from carbonate ores, is of good quality, containing 99.56 per cent. of zinc with a little lead and iron.

China possesses vast deposits of zinc ores, which in the past

have been largely worked by foreign concerns, and the ore exported for treatment, but the erection of smelting works for the treatment of the ore in the country has been proposed, and possibly in the future a zinc smelting industry on modern lines will be established.

Japan.—Zinc smelting in Japan appears to be of recent origin, although zinc ores have been mined in the country for many years and exported to European smelting centres for treatment. The war has, however, given considerable impetus to the Japanese zinc smelting industry, and plant is being erected capable of supplying sufficient metal to meet home requirements and reduce imports of zinc.

The chief smelting works are situated at Osaka and Ohmuta, the former works producing about twice as much zinc as the latter.

The Japanese Bureau of Mines reports the quantity of zinc produced in Japan in recent years as follows :----

Quality.			1914.	1915.	1916.
Refined zinc Unrefined zinc	•••	••	5,966 14,138	21,306 6,121	39,316 2,187
Total	••		20,104	27,427	41,503

PRODUCTION OF ZINC IN JAPAN IN METRIC TONS.

In 1913 the zinc imported into Japan, in the form of ingots and sheet metal, amounted to nearly 11,000 tons, whereas in 1914 it was less than 6,000 tons.

The future of the zinc industry in Japan is generally considered to be exceedingly good, and it is expected that a large export trade will be carried on after the war. One company is manufacturing zinc for the export trade. Much of the Japanese zinc ore contains other metals, such as gold, silver and copper, and the refining of these metals is carried on in conjunction with the treatment of the ore. Five new companies, with a total combined capital of £760,000, have been organised and operate six works for the treatment of zinc ore produced in the country.<sup>1</sup>

<sup>1</sup> Report of H.M. Vice-Consul at Tokio. See Journal of the Society of Chemical Industry, 1917, vol. xxxvi, p. 1119.

According to the *Board of Trade Journal*,<sup>1</sup> the supply of ore for the Japanese zinc smelting works is by no means assured. The production of zinc ore in Japan does not exceed 50,000 tons per annum, whilst the existing Japanese works need about three times this quantity if they are to be kept working at their full capacity. Further, if all the projects for new works and additional plant are realised, the requirements of the industry in the near future for zinc ore will exceed 300,000 tons. This being so, the important question of ensuring a regular supply of ore is now engaging the attention of the zinc smelters and the Japanese Government.

During the past two years zinc ore and zinc concentrates have been imported into Japan from Australia (Broken Hill), China, Burma, Indo-China and Vladivostok, but no contracts for future deliveries of zinc ore appear to have been made.

One important Japanese firm secured during 1916 about 11,000 tons of zinc ore from the Schwai-Ko-Schan mine in China, and recently negotiations have been begun between these two concerns with a view to contracts for the supply of large quantities of ore in the future.

Before the war the cost of zinc production in Japan was nearly 25 per cent. higher than the cost of production in Germany and Belgium, Japan's chief competitors in the zinc industry, and to this cost must be added the cost of transport from those countries to Japan. The total Japanese demand for zinc is estimated at about 29,000 tons yearly, against which Japanese smelting works have a present productive capacity of about 45,000 tons per annum. In the near future, when all the schemes for new undertakings and extensions are completed, Japanese zinc smelting works will have a productive capacity of about 100,000 tons, or 70,000 tons in excess of the requirements of the country. It is stated that schemes are in hand for the establishment of a galvanising industry on a considerable scale, which will absorb some of this excess metal.

<sup>1</sup> October, 1917.

## CHAPTER III

#### ZINC ORES AND THEIR SOURCES OF SUPPLY

### Zinc Ores; Their Nature, Occurrence and Distribution

ZINC-BEARING minerals are geographically very widely distributed—so widely, indeed, that they are found in almost all metal mining districts.

The extent of their distribution is well shown in the accompanying map of the world, in which the more important zinc ore producing districts have been marked.

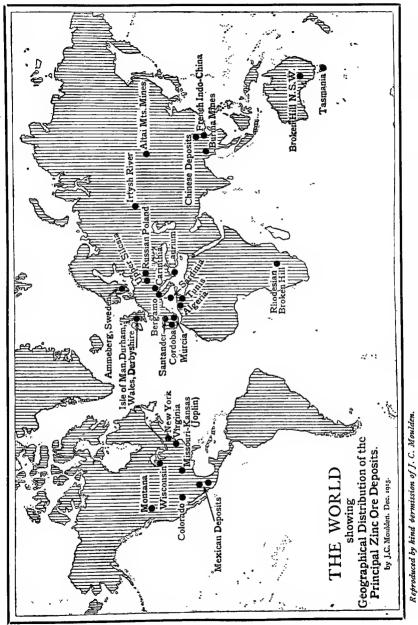
The map was prepared by J. C. Moulden, for his paper before the Royal Society of Arts, and is reproduced here by his kind permission.

The ores of zinc are found more particularly associated with ores of lead, copper and silver, often forming extensive deposits of considerable complexity which present problems to the metallurgist, for the practical solution of which a large number of processes have been devised.

Whilst zinc occurs as a constituent of a very large number of the ores of other metals, minerals containing the metal in sufficiently large quantity, and occurring in sufficient abundance to constitute ores of zinc, are comparatively very few.

The metallurgy of zinc necessitates the employment of ores relatively high in zinc content; it is, therefore, frequently necessary to submit the ores to some preliminary process of concentration to separate the zinc mineral from the other minerals and gangue, or worthless material, before a product sufficiently high in zinc content can be obtained for use by the zinc smelter.

The percentage of zinc in the ore mined is frequently very low, and often averages not more than 3 per cent., but this is increased by concentration to 40 per cent. of zinc or more. ZINC ORES AND THEIR SOURCES OF SUPPLY



Of all the minerals containing zinc, three only are of much importance to the metallurgist; these are the sulphide (blende), the carbonate and the oxidised compounds usually designated under the generic term of calamine, and the silicates of zinc.

Two systems of mineralogical classification are in use for zinc minerals. In this country the carbonate is generally known as calamine, and the silicate as smithsonite or hemimorphite. In America the carbonate is known as smithsonite and the silicate as calamine, whilst the sulphide is commonly called sphalerite. This double classification frequently leads to confusion, especially amongst students.

The American nomenclature of zinc minerals is, however, gradually being adopted by British metallurgists.

The principal zinc-bearing minerals and their respective content of zinc when pure are as follows :—

Mineral.	Composition.	Zinc.
Blende or sphalerite Calamine or smithsonite . Hydrozincite Willemite Hemimorphite Zincite Franklinite	Zinc sulphide	Per cent. 67.15 52.00 57.10 58.10 53.70 80.25 16 to 21

Zincite and franklinite, the composition of which is variable, are important as ores of zinc in the United States of America only and are utilised for the production of zinc oxide.

Although formerly calamine was the most important ore of zinc, blende is, at the present time, the chief source of the metal.

Zinc blende, sphalerite, termed by miners "Black Jack," when pure, contains 67.15 per cent of zinc. It is, however, usually contaminated with iron pyrites and other metallic sulphides, and with gangue minerals, so that as received at the smelting works it usually contains only from 35 to 55 per cent. of zinc.

Regarding its association with galena (lead sulphide), it may be said that most lead mines are also blende producers, and, similarly, nearly every zinc deposit carries lead. The two minerals are frequently mined simultaneously, the blende as a subsidiary source of income to the lead mine.

### Z'NC ORES AND THEIR SOURCES OF SUPPLY

Dressing operations suffice in many cases to yield the greater part of the lead as a galena concentrate, suitable for the lead smeltor, and the zinc blende as a concentrate carrying from 45 to 50 per cent. of zinc.

The lead mines of Cardigan and Cumberland in this country and of Joplin in America, and Broken Hill in New South Wales are familiar examples.

Lead and silver are sometimes present, in the more complex ores, in sufficient quantity to permit of profitable extraction from the residues, after extraction of the zinc.

Germanium has been found to occur in zinc blende from Missouri and Wisconsin<sup>1</sup> The oxide of zinc prepared from zinc residues from the zinc distillation furnaces in which these ores had been treated was found to contain as much as 0.25 per cent. of  $\text{GeO}_2$ .

Zinc blende is very widely distributed and occurs in large quantity in Europe, America, and Australia.

*Calamine*, smithsonite of the Americans, the carbonate of zinc, is decreasing in importance as an ore of zinc since the deposits in many localities are more or less exhausted.

The present supplies are largely derived from Upper Silesia, Austria, Italy, Greece and Algeria.

When pure, calamine contains 52 per cent. of zinc, but it is usually accompanied by oxide of iron, carbonate of lime, etc., which depreciate its commercial value, since these substances give trouble in smelting if present in appreciable quantities. Before smelting, calamine is usually calcined to expel the bulk of the carbon dioxide, thereby decreasing the weight of the ore and relatively increasing the zinc content.

*Hydrozincite* is a basic hydrated carbonate of zinc, the only important deposits of which occur in Spain. Metallurgically speaking, it differs little from smithsonite.

Willemite is anhydrous silicate of zinc, the best known deposits of which occur in Franklin, New Jersey, U.S.A., where it is associated with zincite, franklinite, and calcite, the willemite forming about 25 per cent. of the deposit. It contains, when pure, 58 ro per cent. of zinc, but it is usually accompanied by manganese and other constituents that lower its value materially.

Hemimorphite, electric calamine (calamine of the Americans),

<sup>1</sup> "The Occurrence of Germanium in Missouri and Wisconsin Blendes," G. H. Buchanan, American Chemical Society, 1917.

ς,

a basic hydrated silicate of zinc, occurs associated with the ordinary calamine or zinc carbonate, with lead ores and with blende. It is a valuable ore of zinc, although not of such economic importance as blende or calamine.

It was formerly mined extensively at Aix-la-Chapelle and Moresnet, in Belgium, but these deposits are now practically exhausted. Extensive deposits of exceptional purity occur in Virginia and Missouri, in the United States of America, and provide the source of one of the purest brands of zinc in the world obtained by ordinary distillation methods direct.

Zincite, the native oxide of zinc, known as red oxide of zinc, in a pure condition contains 80.2 per cent. of zinc. It usually contains oxides of manganese, to which the red colour is considered to be due, since chemically pure oxide of zinc is white.

Zincite occurs to a limited extent in the extensive ore deposit at Franklin, New Jersey, forming about 5 per cent. of the deposit.

*Franklinite* is a mixture of oxides of iron, zinc and manganese, of variable composition, but containing as a rule from 12 to 18 per cent. of zinc.

It constitutes about 50 per cent. of the deposit at Franklin, New Jersey. The zinc minerals in this deposit occur as rounded grains in a crystalline limestone, and are probably the result of metamorphism. The willemite associated with the franklinite is separated by a magnetic process and is then treated for the extraction of the zinc.

The franklinite is treated for the production of zinc white (commercial zinc oxide), leaving a highly manganiferous residue, which is smelted in blast furnaces for the production of spiegeleisen, a rich manganese-iron alloy used in the manufacture of steel.

Goslarite, white vitriol, is hydrated zinc sulphate, found chiefly at Goslar in the Harz, and also sparingly in some of the Cornish mines and at Holywell, in Flintshire. The mineral is not, however, sufficiently plentiful to be of much, if of any, commercial importance.

Zinc minerals in small quantity also frequently accompany ores of iron and manganese, especially the latter, from which the zinc, varying from 6 to 10 per cent., is recovered as oxide, in chambers at the top of the blast furnace, when the ores are smelted, thus forming a valuable by-product.

## ZINC ORES AND THEIR SOURCES OF SUPPLY

The zinciferous flue dust frequently contains as much as 75 per cent. of zinc, and is sold to paintmakers or to zinc smelters. The production of zinc from such sources is by no means inconsiderable.

### Zinc Ores in the British Empire

Australia is the premier producer of zinc ore within the British Empire, and in recent years immense quantities have been obtained from this source.

Ores of zinc are also worked in Canada and in the British Isles, and deposits of complex ore in Burma and in Rhodesia are already being actively developed and give promise of becoming a great national asset and of influencing the world's supply of zinc in a marked degree in the near future. Zinc ore is found also in Queensland, Tasmania, New Zealand, Newfoundland, Egypt, Nigeria, South Africa and, associated with copper ore and galena, at Tsumeb, in the former German colony of South-West Africa.

United Kingdom.—The occurrence of zinc ores in the United Kingdom cannot be considered as extensive, although ores of zinc, generally associated with lead ores, are found in the Palæozoic rocks of Wales, the Isle of Man, the North of England and the South of Scotland, some of which have been worked since Roman times.

The best known deposits are those in Flintshire, Cardiganshire, Durham, Cumberland, Derbyshire, the Isle of Man, Dumfriesshire and Lanarkshire. The mines are worked for both zinc and lead, and the ores are subjected to crushing, concentration and separation to obtain a concentrate suitable for smelting.

Formerly calamine was the chief ore mined in the United Kingdom, but at the present time the zinc ore is almost entirely blende, the largest producers being the Nenthead and Nentsbury Mines at Alston, in Cumberland, and the Carshield Mine in Northumberland. Prior to the war the output of dressed zinc ore for the United Kingdom amounted to between 17,000 and 18,000 long tons per annum.

The output in 1913 was 17,294 tons, of which amount England produced 12,730 tons, Wales 2,601 tons, Scotland (Dumfries) 1,010 tons, and the Isle of Man (Great Laxey Mine) 953 tons.

The Alston mines in Cumberland have for some years been

owned and worked by the Vieille Montagne Spelter Company of Belgium, who have installed a very complete up-to-date oredressing plant. The ore produced at these mines, and at one or two other North Country mines, is shipped chiefly to Belgium for treatment. The total weight of British zinc ore exported from the United Kingdom in 1913 was 13,378 tons, of which amount 11,260 tons were consigned to Belgium and approximately 2,000 tons to France.

In 1912 the total export of zinc ore was 11,139 tons. The ownership and working of the British mines by foreign companies, and the exportation of the ore to foreign smelting centres, are not very creditable to the British mining industry, especially when it is remembered that practically all the zinc ore smelted in this country is imported from abroad. Thus in 1913 the total imports of zinc ores by British smelters amounted approximately to 65,000 long tons, which were derived mainly from Australia, Italy, Algeria, Germany, Spain and France.

Attention is now being directed to the possibility of developing the sources of zinc ore in the British Isles, which, with the application of modern methods of dressing and bold development, aided by adequate financial support, may yet be profitably worked. The Development of Mineral Resources Department, recently appointed by the Government, is making a move in this direction.

Canada.—Deposits of zinc ore occur in many parts of Canada and British Columbia, but at present the output is not large. Recent proposals for fostering, by the Government, the zinc industry in the Dominion of Canada will doubtless facilitate the exploitation of known deposits and the search for new deposits.

Practically the whole output in the past has come from British Columbia, mainly from the Kootenay district.

The deposits are numerous, but the ores, which consist of mixtures of argentiferous galena and blende, with or without iron and copper pyrites, are complex and difficult to utilise. Up to the present the zinc concentrates resulting from the treatment of the ores have been shipped to the United States for smelting.

There are prospects, however, that in the near future the ores will be treated in Canada, since the investigations carried out by the Dominion Government on their treatment by electrolytic and other methods have met with some success. During 1913 Canada produced approximately 11,000 tons of zinc ore, almost all of which was raised in British Columbia.

In 1914 the output was approximately 13,000 tons, and in view of the increased mining activity the present output is probably greater.

Australia.—The well-known deposits at Broken Hill, New South Wales, are the most important sources of zinc ore in the British Empire. The ore, which is highly argentiferous, consists of a complex association of galena and blende, with a gangue mainly composed of rhodonite, quartz and garnet.

The ore is crushed and submitted to concentration and separation processes which give two main products, viz., a lead ore concentrate containing 65 per cent. of lead, 6 per cent. of zinc, with varying quantities of silver, and a zinc concentrate containing about 46 per cent. of zinc and 8 per cent. of lead with some 15 ounces of silver per ton. Except for the ore smelted at the plant of the Broken Hill Proprietary Company at Port Pirie, South Australia, and about 20,000 tons annually exported prior to the war to England for treatment, the whole of the zinc concentrates in the past have been sold under long-term contracts to smelters on the Continent. Formerly the ore was worked only for lead and silver, the zinc being neglected, and, as previously stated, it was estimated that in 1903 zinc residues and tailings, containing 18.6 per cent. of zinc, and amounting approximately to 6,000,000 tons, had accumulated at Broken Hill, besides large quantities which had been used for stope fillings in the mines.

After many experiments, these accumulated tailings have, through the application of flotation processes of concentration, become a very substantial source of supply for the world's zinc. The first effect of the introduction of flotation processes on the world's supply of spelter was felt in 1904, and in 1906 the great rise in Broken Hill zinc production began. Between the years 1906 and 1911 the production rose from 100,000 tons of zinc concentrate to roughly 500,000 tons, at about which figure the annual output has since remained. Owing mainly to the high price and scarcity of skilled labour, it has not hitherto paid to smelt these concentrates to any extent locally, or even in the country; they have been bought by European smelters and mainly shipped to Belgium, Germany and France for treatment. The ascertained life of the chief Broken Hill producing mines is such as to assure the future production, although on a gradually reduced scale, for some years to come—probably ten as a minimum—even if no further ore bodies be developed.<sup>1</sup>

Since the outbreak of war the shipments of concentrates has been largely suspended, and the mine owners have had to seek new markets for that very considerable portion of ore that was formerly shipped to the Continent, the contracts with the German firms having been cancelled. Further reference to this matter will be found on p. 200. As stated above, in normal times the output of zinc concentrates is approximately 500,000 tons annually, sufficient to satisfy approximately one-fifth of the zinc requirements of the world in pre-war times. In 1914 the output amounted to only 359,310 tons, being 147,350 tons less than that of the previous year and representing a fall in value of more than  $f_{500,000}$ .

Tasmania.—Lead-zinc sulphide ores occur in the Mount Read district on the West Coast of Tasmania, and although somewhat complex in nature the deposits are being developed with a view to the extraction of the zinc by electrolytic methods, experiments on a commercial scale having proved the feasibility of such treatment. Mount Read is about 17 miles by rail from Zeehan and about 71 miles from the port of Burnie. The zinc-lead sulphide deposits occur over a length of 7 miles and contain from 24 to 43 per cent. of zinc.

Tasmania is expected to play an important part in future development in Australian zinc production.

India.—Large and very promising deposits of silver-lead-zinc ores of the sulphide class occur in Upper Burma. They are situated at Bawdwin in the Northern Shan States, some sixty miles from the Chinese province of Yunnan. The deposits are remarkable for their high silver ratio, and were long ago worked for that metal by the Chinese.

The ore is complex and consists of galena, blende and pyrites with occasional chalcopyrite. The crude ore, as mined, is remarkably free from gangue and frequently contains as much zinc as the Broken Hill concentrates, with substantially greater quantities of lead and silver.

The deposits are being actively developed, and although up to the present they have had little influence on the world's supply

<sup>1</sup> J. C. Moulden, op. cit., p. 502.

of zinc, there is a prospect of this district becoming an important producer in the near future.

South Africa.—A lead-zinc deposit—the Rhodesian Broken Hill—which is reported to be of great prospective importance has been discovered in North-Western Rhodesia. The rich oxidised surface ore consists of a mixture of carbonate of lead with carbonate and silicate of zinc.

The separation of the oxidised ore minerals from one another presents difficulties which have not yet been overcome. But when a commercial process has been worked out and transport facilities have been improved, this, like the Bawdwin deposit, promises to become a valuable addition to the Imperial lead-zinc resources. The deposit is being developed, and a smeltery for lead and zinc is reported to be in course of erection.

The production and value of zinc ore in the British Empire and in foreign countries for the three years 1911 to 1913 are shown in the table on p. 56.

### European Sources of Zinc Ores<sup>1</sup>

The working of zinc ore in Europe in modern times dates from the introduction of the use of brass, and there are records extant which show that in 1439 the calamine mines of Vieille Montagne had been worked for a considerable time by the men of Aix-la-Chapelle.

In the past Europe has contributed very considerable amounts to the world's supply of zinc ores, and although the supply is less than formerly the output is still very large. The bulk of the ore is mined in Germany, and for many years past this country has ranked second only to the United States as a producer not only of zinc ore, but also of spelter. The zinc ore-producing countries of Europe are here referred to in alphabetical order.

Austria-Hungary. — The more important zinc ore deposits are situated in Southern Carinthia, Styria and Tyrol.

The Carinthia deposits are distributed over a wide area, and consist mainly of blende and galena, although large masses of zinc carbonates occur in certain localities, notably at Schneeberg.

In Tyrol, zinc blende has been mined since 1866, prior to which the mines were worked for lead only.

In 1013 the total output of zinc ore in Austria amounted to

<sup>1</sup> The author is indebted to the Bulletin of the Imperial Institute, 1915, vol. xiii, for useful information contained in this section.

		61	1911.	19	1912.	.6I	1913.
		Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
BRITISH EMPIRE :		Metric tons.	Ŧ	Metric tons.	Ŷ	Metric tons.	ŕ
Australia (N.S.W.) <sup>1</sup>	:	516,378	1,414,980	520,518	1,766,242	506,660	1,547,987
Canada	:	2,590	20,840	0,415	44,374	698'4	38,533
Egypt	:	1	I	1,907	1	3,100	] .
India	:	]	0	1	1 0	3,934	4,071
United Kingdom Haioa of South Africa	:	17,052	050,20	17,704	L00'L0	17,294	09,502
FURDE :	:	2	- 6-				
Austria	:	32,166	103,005	34,675	120,202	34,225	1
Belginm	•	836	4,224	1,167	5,660	1,100	I
France	:	43,761	206,360	45,929	208,520	46,577	I
Germany	:	026'669	2,466,200	643,598	2,614,850	637,308	1
Greece	:	37.573	132,890	31,070	I08,520	51,363	I
	:	901	331	777	2,855	406	Ī
9 Italy	:	140,269	615,779	149,776	731,451	158,278	Ī
	:	2,240	2,750	40	50	268	
Russia	:	006'6	Ι,	11,100	1	20,000	ł
Spain	:	162,140	209,700	175,311	306,827	174,831	I
Sweden	:	88,779	315,240	83,558	313,636	50,752	I
ASIA :		¢	, ,				
China <sup>2</sup>	:	4,780	6,982	7,170	LL1'L1	9.550	I
Indo-China	:	28,24I	103,693	28,400	140,040	]	I
Japan	:	23,582	82,583	35,741	106,813	45,200	I
NORTH AFRICA :		0.0	262 022		80.0.0	9-0-00	
Algena	:	00,429	303,005	74,000	404,240	067.20	I
N P. C. A	:	27,900	113,080	37,400	224,400	30,300	I
3			011	20			1
	:		7CT	10 2	90	- 611	
Douvia	:	6,790	662.67	106'0	20,400	110%	I
Mexico	:	40,181	90,841	40,743	01,920	20,000	
United States	:	240,413	0,358,274	293,847	9,178,474	11,740,595	(Tucindes
							1,291,712 tonsof zinc- lead ore)
* Compiled from various sources.	ces.	<sup>1</sup> Concentrate	<sup>1</sup> Concentrates and Spelter.		<sup>2</sup> Exports only.	<sup>3</sup> Including lead ore.	ad ore.

## THE ZINC INDUSTRY

THE WORLD'S PRODUCTION OF ZINC ORE.\* (METRIC TONS, 2,2c4.6 LB.)

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31,000 long tons; of which about one-half was devoted to Government use. The annual output has remained about the same for the past five years.

Hungary cannot be classed as a zinc ore producer, as mining for the metal is almost unknown.

Belgium.—In the early days of the zinc industry Belgium was an important producer of zinc ore, but since 1856 the output has been comparatively insignificant, owing to the gradual exhaustion of the rich deposits.

The most important zinc mines are at Bleyberg, and near Verviers and Liége, whilst the famous deposits worked by the Société de la Vieille Montagne are, as previously stated, situated in Moresnet.

The Bleyberg ore consisted chiefly of zinc blende and galena in nearly equal amounts, whereas the deposits of Vieille Montagne consist chiefly of smithsonite and hemimorphite, but large masses of the silicate, willemite, are also occasionally found. Very little zinc blende accompanies these ores. Zinc ore has also been mined at Welkenrodt near Altenberg, Nouvelle Montagne, Corphalie near Liége, and Philippeville, from which districts large quantities of ore have been mined in the past.

The present output of zinc ores (entirely blende) from the Belgian mines is about 11,000 long tons per annum.

Bulgaria.—This country is a small zinc ore producer, the chief source being the Sedmolchisleniza Mine, about six miles southwest of Vratza. The crude ore contains about 18 per cent. of zinc, but by hand-picking the zinc content can be raised to 28 per cent.

Ores are also worked at Roupio and at the Blagodat Mine near Kustendil.

France.—This country first became a zinc ore producer about 1870, the ore consisting chiefly of carbonate, being obtained from the country between the Alps and the Pyrenees. Within recent years the supply of zinc ores has fallen considerably. The largest producing mines at present are those of Malines (Gard), where zinc ores have been worked since 1883. Both oxidised ores and blende are worked.

In the Pyrenees, zinc ores occur in many localities. Argentiferous sulphides and carbonates of zinc and lead are produced at the Sentein mines in Ariège, and important deposits also occur in both the Hautes and Basses Pyrenées. Deposits of zinc carbonate, silicate, and blende occur in the department of Var, the chief mine being the Bormettes, which produces zinc blende. The total output in 1913 amounted to only about 45,000 long tons, compared with 95,000 long tons in 1909, more than one-third coming from the mines at Malines.

The French colonies Algeria and Tunis are also important zinc ore producers and may be conveniently considered here. In Algeria, both zinc carbonate and blende are worked in the department of Constantine. The chief mines are the Hammam N'Bails and Ain Arko. Ore is also mined at several places near the Atlas Mountains. In 1913 Algeria produced 81,000 long tons of zinc ore, chiefly calamine, compared with 83,000 long tons for the previous year.

Tunis produces about 35,000 long tons of zinc ore annually, consisting chiefly of carbonate and silicate, derived from a number of localities. The ore is usually calcined locally before being exported in order to save freight.

In the past, most of the ore produced in Algeria and Tunis was shipped from the ports of Bona and Sousse, and found its way to smelters in Belgium, France and Germany.

Germany.—This country is the chief producer of zinc ore in Europe, the most important deposits being situated in Upper Silesia, whilst ore in smaller quantities is obtained in Rhineland, Westphalia, Nassau, the Harz, etc. Although mined for centuries, the German zinc deposits still produce a considerable amount of high grade ore.

The well-known deposits of Upper Silesia occur in the southeastern corner of the province, on the borders of Austria and Russia. The ores of this district are principally calamine and blende. The latter occurs in the deeper workings, consequently as the mine workings increase in depth the proportion of calamine as compared with blende has gradually declined.

The calamine occurs rarely in the condition of pure zinc carbonate; the bulk of the ore is in the form of a dolomitic calamine, often more or less argillaceous. The deposits are very irregular, and occur in the form of more or less extensive pockets, whilst the blende deposits show great continuity.

Oxidised ores were treated exclusively in the Silesian district until about 1860, but since that time blende has been worked in increasing quantity and is now by far the more important ore smelted in the district. The crude zinc blende, as sent to the dressing plants, contains, on the average, about 10 per cent. of zinc, but dressing gives a high-grade smelting concentrate.

The calamine produced in Upper Silesia is usually ferruginous and of high grade, containing from 28 to 35 per cent. of zinc; cadmium in appreciable quantity is usually present. Ores containing as little as 13 per cent. of zinc are worked in Silesia by local smelters, such ore being of too low grade to bear the cost of transport. As a general rule, the zinc ores smelted in Silesia are of very low grade.

In Westphalia, the ore is mainly blende, the chief deposits occurring at Iserlohn and Brilon.

In the Upper Harz and Hanover, zinc blende is recovered in the dressing of argentiferous lead ore mined near Clausenthal and Laurenthal.

In the Lahn Valley, Nassau, important deposits of more or less complex sulphide ores occur, carrying about 3 per cent. of zinc, 4 per cent. of lead, and 2 oz. of silver per ton.

The crude ore is concentrated at the Laurenberg, Silberau and Friedrichssegen works, and yields a blende concentrate containing 44 per cent. of zinc, and a galena concentrate with 36 per cent. of lead and 11 oz. of silver per ton.

The Lower Harz deposits occur chiefly at Rammelsberg, near Oker. The ore is an intimate mixture of zinc blende with other metallic sulphides, and yields on concentration a product carrying 25 per cent. of zinc.

Special processes have been devised for the treatment of the Rammelsberg ore body (see p. 110).

At the present time, the larger proportion of the zinc ore mined in Germany comes from the Silesian district, the output, which has steadily declined in recent years, amounting to between 650,000 and 700,000 long tons per annum. In 1913 the production amounted to 627,000 long tons, a decline of about 10,000 tons on the previous year. This decrease in output is, however, most probably intentional, since Germany, as previously stated, has for some years adopted the policy, which is being strictly followed, of conserving national resources of ore. It is due to this fact that Germany has been able to maintain a considerable output of zinc during the war, in spite of the cutting off of imported ores.

Greece.—The most important zinc mines are those of the

Laurium district, where both zinc blende and carbonate occur. The mines are of great antiquity and still yield a considerable amount of ore. The carbonate ore is usually calcined before export, and then contains about 60 per cent: of zinc. The production in 1913 consisted of about 30,000 long tons of blende and 20,000 long tons of calcined calamine a total of 50,000 long tons, showing a decrease of some 17,000 long tons on the previous year.

Italy.—Zinc carbonate ore is mined chiefly in Sardinia, the carbonate of which has long been famous. The mines now worked are amongst the most productive in Europe. Less important deposits occur in Lombardy, Piedmont and Tuscany. The richest mines in Sardinia are probably those of the Inglesias district, which yield zinc carbonate and silicate near the surface, whilst zinc blende is found at the lower depths.

The output was approximately 151,000 long tons in 1913. The ore has hitherto been exported chiefly to Germany, Belgium and the United Kingdom. Important zinc mines in Sardinia have long been operated by the English Crown Spelter Company, of Swansea, to which port the ore is shipped for treatment.

Norway.—Small amounts of zinc ore have been mined at Hadeland, Modum, and Ranen. Extensive deposits of lowgrade ore occur near Christiania, but their concentration has presented considerable difficulty.

Russia.—Russian Poland, in the districts bordering on Silesia, produces calamine from deposits which are probably an extension of the Silesian deposits in Germany. At one time the zinc deposits of Poland were amongst the most productive in Europe.

Several deposits of complex ore containing zinc occur in the Nerchinsk district of Eastern Siberia, and in the Altai Mountains, Siberia, in the Irtish River district. These districts are being developed, with the aid of British capital, and promise to become of importance in the future.

In the Northern Caucasus, rich deposits occur at Sadon and Primorsk, the latter being mined by the Tetysch Company.

The output of the district in 1910 was about 20,000 tons.

Spain.—The most important zinc ore deposits are found in the provinces of Murcia and Santander, which produce about 80 per cent. of the total Spanish output.

Small amounts are obtained from deposits in the provinces

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of Teruel and Cordoba. About 175,000 long tons of ore, both calamine and blende, are mined annually in Spain, a small portion only of which is smelted in Spain, the remainder being shipped to Belgium, Germany and France.

Sweden.—The only important mines appear to be those at Ammeberg, in the Nerike province. The mines, which are controlled and worked by the Vieille Montagne Company, are situated about eight miles from Ammeberg, at the northern end of Lake Wetter. The ore consists of zinc blende, associated with pyrites and galena, and after hand-sorting carries about 20 per cent. of zinc and I per cent. of lead.

In order to facilitate the removal of the pyrites the ore is slightly roasted before being crushed and concentrated. The concentrates, as shipped, contain about 42 per cent. of zinc, and have hitherto been treated in Belgium.

The output in 1913 was 50,840 long tons, practically the whole being blende.

Moulden has stated that many of the iron mines yield also no small amounts of zinc blende, and under favourable conditions the potentialities of this country are undoubtedly considerable.

### American Sources of Zinc Ore

The United States of America is the greatest producer of zinc ores in the world, the output at the present time far exceeding that of any other country.

The output in 1913 approximated to no fewer than 790,000 long tons, exclusive of ore exported or used for the manufacture of zinc oxide. Since the outbreak of war the output has increased enormously.

Both calamine and blende are extensively worked, in addition to the zincite and franklinite deposits. There exist also great reserves of the more complex low-grade lead-zinc ores, which, owing to the abundance of richer and purer ores, have not yet been exploited to any considerable extent.

Of the recoverable zinc content of the ores mined in 1913, more than 77 per cent. was contained in zinc ores proper, the remainder, with the exception of 0.8 per cent., being from zinclead ores.

The chief ore-producing States in order of importance are Missouri, Wisconsin, Idaho, Kansas, Oklahoma, Colorado and

#### THE ZINC INDUSTRY

Montana, but there are in addition some twelve other States that produce smaller quantities of zinc ore and collectively considerably augment the output for the United States.

The mine production of zinc-yielding ores in 1913 from the more important States is shown in short tons (2,000 lb.) in the following table :---

State.		Zinc Ore.		Zinc-lead		
		Crude Ore.	Zinc Content.	Crude Ore.	Zinc Content.	Total.
		Short tons.	Per cent.	Short tons.	Per cent.	Short tons.
Missonri		8,049,300	1.6	-		8,049,300
Wisconsin		1,406,000	2.1	-		1,406,000
Idaho	••	2,719	42.2	646,080	1.6	648,799
Kansas	••	590,300	1.7	I →		590,300
Oklahoma	•••	581,000	2.0	-		581,000
New Jersey	••	490,434	17.2			490,434
Colorado	••	141,295	23.5	203,367	11.4	344,662
Montana		3,840	9.8	307,615	14.3	311,455
Utah		16,322	29.2	211,609	2·1	227,931
Tennessee	• •	171,392	3.3		—	171,392
New Mexico	••	40,439	17.0	8,735	16.1	<b>49,</b> 174
Arizona	••	14,554	17.2	29,700	7.3	44,254
Nevada	••	10,208	31.1	16,749	24·I	26,957
Totals	••	11,517,803		1,423,855		12,941,658

ZINC ORE PRODUCTION IN THE UNITED STATES, IN SHORT TONS .(2,000 LE.), IN 1913.<sup>1</sup>

These figures show that the zinc content of the ores as mined varied from as little as 1.6 per cent. to 42 per cent., these figures being the average for Missouri and Idaho respectively; the average for the whole of the crude zinc ore mined in 1913 was 2.8 per cent.

The low-grade ores are submitted to concentration processes, and so far, in the United States, the greatest tonnage of zinc concentrates has been produced by magnetic separators, without including the enormous separating plant at Franklin Furnace, New Jersey, with its capacity of nearly one thousand tons daily, for the separation of franklinite from willemite. Flotation processes are, however, now being introduced for the treatment

' United States Geological Survey and Department of Mines Report, 1914.

of complex ores in America. Detailed reference must be restricted to the more important zinc ore-producing States in their order of quantity of ore mined.

 $\dot{M}$ issouri.—Output 8,049,300 short tons. Although the zinc deposits of Missouri consist of some of the lowest grades of zinc ores worked in the country, the enormous output enables the State to hold the first place as regards zinc production. The ore mined is mainly zinc blende with small quantities of galena and marcasite.

About three-quarters of the celebrated Joplin district is in Missouri, the remainder being in Kansas (Cherokee County) and Oklahoma (Ottawa County).

The zinc-bearing deposits of the Joplin district consist of large pockets from which ore can be removed cheaply and in a more or less crude manner.

The character of the ore is such that, in practically all cases, it breaks away from the gangue material easily with coarse crushing, and makes an ideal jig product, any lead contained in the crude ore being saved by the jig as a separate product, which is sent to the lead smelter. The bulk of the ore now mined in this district is blende, calamine forming about one-tenth only of the total output.

Important deposits of "silicate ore" (a mixture of hemimorphite and smithsonite) occur in the Aurora and Granby districts; in many cases the ore contains from 40 to 45 per cent. of zinc, and is therefore of sufficiently high grade to ship in lump form.

Wisconsin.—Output 1,406,000 short tons. As a zinc ore producer this State ranks second, but occupies fourth place as regards zinc output. The most important ore-producing counties are Grant, Iowa, and Lafayette.

The ores, which consist of galena, zinc blende, and smithsonite, contain a large amount of marcasite, and much difficulty was at first experienced in concentrating the ore, but this has been overcome by slightly roasting the ore to render the marcasite non-magnetic.

By this means magnetic separation of the blende from its associated iron sulphide is rendered possible, thus giving a shipping ore of sufficiently high grade suitable for distillation. In 1914 there were 46 ore dressing mills and five magnetic separating plants in operation in various places in the Wisconsin district.

Zinc carbonate ore also occurs in Wisconsin, mainly in the

Highland and Mineral Point districts, and it is chiefly used for the production of zinc oxide.

*Idaho.*—Output 648,799 short tons. Zinc-lead ore is chiefly mined in this State and is obtained from the Beaver, Hunter and Placer Center districts of Shoshone County.

The zinc content of the ore as mined is about 2 per cent., but concentration yields a product containing on an average 34 per cent. of zinc and small amounts of gold and silver, which enhance the value of the ore.

A small quantity of crude ore of good quality and containing about 42 per cent. of zinc was shipped from the Beaver, Summit and Lelande districts in 1913.

Kansas.—Output 590,300 short tons. Practically the only deposits at present being worked in this State are those of Cherokee, in the south-eastern part of the State, which forms the western portion of the Joplin district.

Both carbonate and sulphide of lead occur with the zinc ores, which are of low grade and contain on an average about 1.7 per cent. of zinc only.

Oklahoma.—Output 581,000 short tons. The zinc ore deposits in Ottawa County in this State form the south-western portion of the Joplin district. The Miami district is responsible for about 95 per cent. of the total output in Oklahoma. The crude ore as mined contains a little more than 2 per cent. of zinc, but yields a concentrate suitable for smelting.

New Jersey.—Output 490,434 short tons. This State is of considerable interest on account of the special nature of the zinc minerals in the ore.

Practically the whole of the output is obtained from two deposits that occur in Franklin Furnace and Stirling Hill, in Sussex County, both of which are mined by the New Jersey Zinc Company. Enormous quantities of the ore are consumed annually in the manufacture of zinc oxide direct from the ore, so that in 1913 New Jersey only attained fifth place on the basis of zinc produced.

The ore comprises zincite, willemite and franklinite, but the relative amounts of the minerals vary considerably. The franklinite is usually closely associated with the other zinc minerals, from which it is separated by magnetic treatment, first devised by Samuel Wetherill, who also developed and applied the blowing-up grate furnace for the economic production of zinc oxide direct from these ores. The name of Wetherill thus became intimately associated with the history and success of the district.

Colorado.—Output 344,662 short tons. Zinc ore is mined in many localities in this State. About 80 per cent. of the zinc ore produced in the State is derived from the Leadville mines in Lake County. The deposits yield galena, zinc blende, and iron pyrites, the crude ore containing 19 per cent. of zinc. Considerable amounts of zinc carbonate and silicate are also mined in this district. In 1913 the output consisted of approximately 98,000 tons of crude sulphide ore and 136,000 short tons of carbonate and silicate ore.

The next largest producing counties are Eagle and Summit, their total output in 1913 being about 8 per cent. of that of the whole State. In Summit County zinc blende is associated with galena, but usually the quantity of galena is small. The ore as shipped is stated to contain 42 per cent. of zinc.

Other zinc ore-producing counties are San Miguel, Dolores and Chaffee.

Montana.—Output 311,455 short tons. The zinc ore produced in this State comes largely from the celebrated copper district of Butte, the chief mines being the Butte and Superior. The Butte district, which has very rapidly come into prominence as a zinc ore producer, promises to become one of the largest zincproducing areas in the United States.

The ore is chiefly zinc blende and carries about 20 per cent. of zinc, but by concentration a product is obtained carrying 49 per cent. of zinc and about 24 oz. of silver per ton and a little gold. In 1913 Montana was third as a zinc producer.

Utah.—Output 227,931 short tons. The ore produced in 1913 was derived chiefly from Beaver County, whilst important outputs were made from the counties of Salt Lake, Utah, Wasatch, Summit, Tooele and Juab.

The zinc-lead ores contained on an average about 27 per cent. of zinc and 0.06 oz. of silver per ton, but concentration yielded a product containing about 33 per cent. of zinc and nearly 2 oz. of silver per ton.

Tennessee.—Output 171,392 short tons. During the past few years there has been considerable activity in prospecting zincbearing deposits in Eastern Tennessee, and several large bodies of ore have been located. Zinc blende is mined in Knox County, the zinc content of the crude ore being from 3 to 5 per cent; the concentrate obtained from this carrying about 60 per cent. of zinc.

New Mexico.—Output 49,174 short tons. The production in 1913 was chiefly from mines in the Socorro, Luna and Grant Counties. The ore shipped in 1913 consisted of 12,000 short tons of zinc blende and concentrates containing 42 per cent. of zinc, and 13,000 short tons of carbonate ore containing 34 per cent. of zinc.

Arizona.—Output 44,254 short tons. Most of the ore mined in this State is obtained from Mohave and Pima Counties. Small amounts are also produced in Yavapai and Cochise Counties. Both zinc and zinc-lead ores are produced, the latter forming about two-thirds of the total output.

Nevada.—Output 26,957 short tons. The ore raised in this State in 1913 consisted of zinc-lead ore and of silicate and carbonate; it was chiefly produced in Clarke and Lincoln Counties. The ore as sold to the smelter averaged about 30 per cent. of zinc.

*Mexico.*—Zinc ore occurs in a number of localities in Mexico, but many of the deposits cannot be utilised owing to transport and other difficulties.

The chief producing States are Coahuila, Chihuahua, San Luis Potosi, Tamaulipas and Nuevo Leon.

The bulk of the ore mined in the past has been exported to America and to Europe, but in recent years the unfortunate political disturbances prevailing in the country have prevented ore producers from taking advantage of the more favourable import duties on ores entering the United States.

Conditions limiting the shipment of zinc ore from Mexico have now improved somewhat, so that a larger output of ore than in past years is to be expected.

In 1909 the ore imported by America from Mexico amounted to 105,000 short tons, but since that time the output has fallen considerably, amounting to only 18,000 short tons in 1913 and 21,000 short tons in 1914.

The ore shipped usually contains from 30 to 40 per cent. of zinc and varying amounts of silver.

South America.—This continent is at present a very small zinc ore producer, Bolivia and Peru alone making small contributions.

Bolivia.-The present output is derived chiefly from the

Huanchaca district, but zinc ores have been found in a number of other localities in Bolivia.

Owing to shortage of water for concentrating the ore and to other difficulties, the output has decreased in recent years. The production in 1913 was 7,500 short tons, and in 1914 it had decreased to approximately 4,000 short tons.

An estimate of the total production of zinc ore in the United States is given in the report of the zinc smelters, who are stated to have smelted in 1914 approximately

> 629,000 short tons of blende. 227,000 ,, ,, of calamine.

Total .. 856,000 short tons.

This total will probably include some 21,000 short tons of ore imported from Mexico and 11,000 short tons from Canada.

On the other hand, a small quantity of ore, amounting to 11,000 short tons, was exported to Europe.

The very considerable increase of zinc ore production in America since the outbreak of war is shown by the following figures, which give the recoverable zinc content of the ore mined in the United States for the past four years.<sup>1</sup> In 1913 it was 406,000 short tons; in 1914, 407,000 short tons; in 1915, 605,915 short tons, and in 1916, about 708,000 short tons. The large increase in output in 1915 and 1916 was due to the demand for zinc from Great Britain and the Allies.

The largest increase in output was made by the Joplin region, which in 1916 had an increase of more than 40,000 short tons. Montana made a notable increase and from the return available appears to have taken second place. Substantial increases were also made in the zinc mining districts of the Upper Mississippi, Valley, Colorado, Tennessee, Idaho, Nevada, New Mexico, New York, Arkansas and Washington.

Of the total output of zinc in the ore mined, the Eastern States produced 148,000 short tons, or 21 per cent.; the Central States 274,000 short tons, or 39 per cent.; and the Western States 286,000 short tons, or 40 per cent.

# Asiatic Sources of Zinc Ores

Little accurate information appears to be available regarding the nature and extent of many of the zinc deposits in Asia.

<sup>1</sup> United States Geological Survey Report.

Actual figures of output are also very difficult to ascertain. China has long been the largest zinc ore producer in Asia, but in recent years considerable attention has also been given to zinc deposits in Japan and Siberia.

*China.*—This country appears to have been the world's earliest producer of zinc ores, and also of metallic zinc produced by crude methods of native smelting.

The most important deposits worked are situated in the Prefecture of Changlin, in Hunan province, and consist of argentiferous galena, associated with blende, iron pyrites and calcite. The deposit has been exploited by means of surface workings for about two centuries, and has been considerably developed during recent years as the result of German influence. The chief mines are the Shui K'ou Shan, worked by the Hunan Board of Mines.

A considerable portion of the ore mined is first submitted to a preliminary dressing at the mine. The dressed blende and mixed zinc-lead sulphides are then sold to a German firm having an ore-dressing plant at Woo Chang, where the material is further concentrated to yield a zinc concentrate carrying from 30 to 35 per cent. of zinc, which prior to the war was exported to Germany to be smelted.

It is stated that before the outbreak of war the German company was considering the desirability of erecting a smeltery in China. The output of zinc ore in 1914 was approximately 21,500 long tons.

Numerous deposits of zinc ore are known to occur also in South-Western China, and in Kweichow province appreciable quantities of metallic zinc have been produced by native smelting.

Japan.—Zinc blende, usually associated with ores of copper and lead, has been found in a number of localities in Japan, but up to the present most of the marketable ore has been obtained from the Kamioka Mines in the province of Hida, the output of crude ore being normally about 10,000 long tons annually. The crude ore, consisting of zinc blende and argentiferous galena carrying from 10 to 16 per cent. of zinc, is treated at two dressing works at Shikama and Mozumi, where wet concentration and flotation methods are employed. The greater part of the zinc concentrates produced have in the past been exported, chiefly to Belgium.

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The lead concentrates are smelted in blast furnaces about 35 miles from Toyama.

Zinc mines of less importance occur in the provinces of Tsushima, Etchu, Echizen, Bizen and Mimasaka.

The output of zinc ore within the Japanese Empire has shown a very marked increase during recent years, practically the whole of which has been exported to foreign smelting centres for treatment. Thus the exports amounted to approximately 18,000 long tons in 1909, to 22,000 long tons in 1910, and 23,000 long tons in 1911. The annual production at the present time is said to be about 50,000 long tons.

Japanese zinc ore amounting to 1,200 long tons was imported into the United Kingdom in 1913 and more than 5,000 long tons in 1914.

In view of the great activity in the Japanese zinc industry since the outbreak of war, and the erection of smelting plant to smelt the zinc ores mined in the country, the mine-owners would appear to have a very hopeful future before them.

Siberia.—Important deposits are worked at the Ridder Mine in the Altai Mountains, Siberia. Since the mine was acquired by the Irtish Corporation, Ltd., in 1915, considerable development has taken place. The ore produced is said to consist of two qualities, about one half being high-grade ore containing 27 per centrof zinc, 18 per cent. of lead, and 1 oz. of gold per ton. whilst the remainder is of lower grade, carrying about 9 per cent. only of zinc and 5 per cent. of lead. As previously stated, the Irtish Corporation are building a large zinc-and-lead smelting plant at Ekibastus for the treatment of the ore of the Ridder Mine. Part of this plant began operations in May, 1916.

### CHAPTER IV

#### THE MARKETING OF ZINC ORES

### The Concentration of Zinc Ores

ORES of zinc as mined are seldom of sufficiently high grade to be sent direct to the smelter for immediate conversion into metal without previous concentration. Especially is this the case with ores containing zinc blende, which is by far the most important source of zinc at the present time.

The gradual exhaustion of the deposits of rich calamine ores has led, during the past few decades, to a considerable development in the concentration of zinc blende ores to meet the demand of the smelters for high-grade ores.

During the past twenty years the zinc ore market has been considerably augmented by the supply of thousands of tons of "zinc concentrate," a high-grade zinc blende product resulting from the mechanical treatment of low-grade ores, and so-called complex ores, in which the zinc is intimately associated with other metals, such as lead, copper and silver.

The preliminary treatment of zinc ores has for its object not only the enrichment of the ore by removal of the minerals of comparatively low specific gravity which compose the gangue, but also the elimination, as far as possible, of heavy minerals, such as those containing lead, iron and manganese, which are objectionable in smelting.

In many cases these heavy minerals are of market value and are recovered in sufficient quantity to be a source of profit.

The methods of concentration employed include hand sorting and separation by gravity (wet dressing), electromagnetic and oil flotation processes, or combinations of these. The process adopted varies with the nature of the ore.

Where ores are sufficiently high in zinc blende and lead

(galena) and carry little or no iron pyrites, or chalcopyrite, the ordinary methods of water concentration in jigs, and upon tables, such as are employed at Joplin and some of the Leadville mines in the United States, give satisfactory separation, but magnetic separation or flotation methods are usually employed for more complex ores. In favourable circumstances, and if worked on a sufficiently large scale, ore containing as little as 3 per cent. of zinc may be worked at a profit, and will on concentration yield a zinc product suitable for smelting; but in such cases the lead and copper, and small amounts of silver and gold which often accompany the zinc in the ore, are recoverable, and are usually the determining factors of commercial success in the treatment of low-grade ores.

In this connection, the more modern system of concentration known as "flotation," which is applicable to the treatment of the sulphide ores of most metals, has in recent years been widely adopted for concentrating those of zinc.

Magnetic concentration has been successfully applied to the separation of the zinc minerals comprising the well-known franklinite ores of New Jersey.

Following the pioneer work of Wetherill's high intensity magnetic separator, considerable progress has been made in the magnetic concentration of ores, and many machines have been introduced. Electrostatic methods for the separation, by electric repulsion, of good conductors (such as certain metallic sulphides, magnetite, hæmatite, etc.) from poor conductors (such as silicates, carbonates, oxides and sulphates, and including zinc blende) were first applied in practice by Blake and Mechernich, and followed by Sutton and Steele, Huff and others.

Magnetic separation of blende and pyrites may be accomplished without preliminary roasting by the use of high intensity magnetic separators of the Wetherill type, the zinc mineral being lifted out of the mass.

The more usual practice, however, is to give the mineral a magnetic or "flash" roast, rendering the iron magnetic, after which it is separated from the mass by separators of the low intensity type, such as that of Dings.

The main objection to electric separators appears to be their inability to handle fine powders, and their liability to dust trouble unless the dust be first removed.

The flotation processes of concentration have come rapidly

to the front since their introduction some fifteen years ago by the Messrs. Elmore. Their work, which resulted in the filing of Frank Elmore's patent in 1898, focussed the attention of metallurgists upon the great possibilities of these methods.

Many new systems of concentration by flotation have been introduced within recent years.

In these processes advantage is taken of the property possessed by metallic sulphides, when in a fine condition, of floating in water, hence their term of "flotation" processes. When for example, a mixture of such sulphides and waste mineral (gangue), in a finely crushed condition, is gently brought on to the surface of moving water, it will be found that the sulphide particles will float, whilst those of the gangue will break through the surface and sink. This different behaviour will be augmented if the water be very slightly acidulated, and still more so if the surface of the sulphide particles is oiled or greased. Since metallic sulphides possess also the property of absorbing oil, or being " wetted " by oil, while particles of gangue do not, a separation can be effected by agitating the finely crushed ore with water containing a small proportion of oil, whereby the sulphide particles will gradually collect in the floating film of oil, whilst the rock particles remain sunken.

Neither of the above phenomena alone suffices for a practical working method; other principles equally important have been drawn upon (such as the modification of the surface-tension of water, factors of absorption, aeration, fine subdivision of the mineral, etc.) and blended into one or other of these processes, which reverse the operations of "wet" concentration inasmuch as they save the heavier mineral by floating it to the surface whilst causing the specifically lighter material to sink.

In the Elmore oil vacuum process separation is assisted by the partial exhaustion of a large metal receiver into which the oiled slimes and water enter. The air films surrounding the oiled particles are thus expanded, and the separation is much improved. In other cases diluted acid is employed, and with suitable ores gas bubbles are produced which cause the sulphide particles to rise to the surface of the liquid.

One of the most widely used and successful of the flotation methods of concentration is that known as the "Froth Flotation Process," wherein the mineral is recovered in a more or less thick and coherent bubble-froth which is skimmed or run off from the pulp, thus effecting a separation of the mineral from the gangue.<sup>1</sup>

The success of flotation methods has been very marked in the treatment of large quantities of slimes and complex ores that had previously defied all known methods of treatment.

They proved to be very suitable for the treatment of the complex ores obtained from Broken Hill, New South Wales, in which zinc blende and galena are very intimately associated, and enormous quantities of these and similar ores are now treated by flotation.

By gravity concentration it was possible to market only about 60 per cent. of the lead in the Broken Hill deposits, and less of the silver, leaving the bulk of the zinc associated with the heavy waste as a middle product, whilst the finest and lightest portion of the crushed material was often allowed to flow away.

So successful has been the application of flotation methods to the treatment of the Broken Hill ores that now the whole range of zinc products is treated by flotation, and zinc concentrate to the extent of about 500,000 tons per annum is being recovered.

Owing principally to improved methods of mechanical separation, large deposits of zinc-lead sulphides are being opened up in America, Burma and Siberia, in addition to those in Australia and elsewhere.

In view of the fact that the supply of flotation and other zinc concentrates is bound to increase, metallurgists are giving special attention to their treatment, since in many cases their very fine state of division renders some modification of the ordinary smelting processes necessary.

### The Valuation of Zinc Ores

For technical purposes, zinc ores are divided into two classes : (1) zinc blende, and (2) calamine, the latter including the common carbonates and silicates.

A large proportion of the zinc ore now marketed consists of zinc blende concentrates, which usually contain from 35 to 55 per cent. of zinc.

The market value of an ore is based on the price of the metal content, less the total cost of extraction; in other words, the net return to the proprietors.

The zinc content is determined by wet analysis, usually

<sup>1</sup> "Copper," H. K. Picard, London, 1916, p. 24.

volumetrically by sodium sulphide (Schaffner's method) or by ferrocyanide.

The value of a zinc ore depends chiefly upon its content of zinc and the absence of objectionable impurities such as iron, manganese and lime (calcium carbonate), which form fusible slags and increase the corrosion of the retorts; and lead, cadmium, arsenic and antimony, which contaminate the spelter and therefore lower its market value. Lead, however, is present in almost all zinc ores.

The total percentage of iron and manganese should not exceed 10 per cent., and if lead is present the metallic zinc produced by distillation will be contaminated with lead unless special precautions are taken.

Fluorite (calcium fluoride) is sometimes present and is a very undesirable constituent, as it forms a very fusible slag, and when present in appreciable quantity in zinc blende causes deterioration in the lead chambers used in the manufacture of sulphuric acid as a by-product from the roasting of the ore.

The value of the ore is also affected by its character, whether oxidised or sulphide, or a mixture of both; the sulphide ore must be roasted, but yields a diminished weight for the subsequent treatment, which is the most expensive part of the process; the calamine ores seldom require preliminary treatment by the smelter, as the economy in freightage between mine and smelter is usually sufficient to warrant calcination to expel carbon dioxide and combined water prior to shipment, this saving being more important where the mine is widely distant from the smelting works.

The value of an ore is, moreover, affected by its physical condition. Lump ore is subject to an additional expense for crushing : fine concentrates are more expensive and troublesome to treat than coarse concentrates.

Some ores roast and distil easily, others with more difficulty. All these factors are considered by the zinc smelter in purchasing ores.

It will be observed, therefore, that whilst the chemical composition of ores is the most important factor in determining their value, the price does not depend solely on the metallic content and on the presence of other compounds, but also on certain physical properties governing the suitability of the ore for smelting purposes or for other methods of treatment. Several schedules are employed in Europe for calculating the value of zinc ores, all of which embody at least three factors: (I) the current price of spelter, (2) the zinc content of the ore, (3) a " returning charge " per ton of ore.

The last named is the cost of smelting a ton of ore, and is affected by the mineralogical nature of the ore and its physical condition. The treatment charges necessarily vary in different smelting centres, as, in addition to the above factors, they are also affected by local conditions, such as fuel supply, cost of labour, freight, etc.

A general type of formula used for calculating the value of zinc ores is as follows:

$$V = 0.95 P\left(\frac{T-8}{100}\right) - R,$$

Where V is the value in f per ton,

P the price of spelter (G.O.B.) in London,

T the percentage of zinc in the ore,

R the " returning charge."

The selling price basis for London spelter (G.O.B. = good ordinary brands) is usually the average of the daily prices for the month previous to arrival, and is usually taken as London Public Ledger quotation less 5 per cent., which is, of course, 0.95 Pof the formula. Thus on a £20 average quotation basis the ore unitage paid for (T-8) is based on 95 per cent. of £20, which is £19, or 3.8 shillings per unit.

As an example of the use of the above formula, if an ore which contains 48 per cent. of zinc and spelter is £30 per ton in London, and if a returning charge of £3 5s. be assumed, then the market value of the ore per ton will be:

$$f_{0.95} \times 30 \left( \frac{48-8}{100} \right) - f_{3.5} = f_{8.3} = 0$$

When silver is present in the ore in sufficient quantity to permit of profitable extraction, it is usually paid for at the price based on the current price of standard silver after allowing for smelting loss and for cost of working.

In determining the treatment charge on the ore purchased, the zinc smelter starts with the cost of smelting a ton of the ore of average composition, that is to say, the mixture on which he proposes to operate his furnaces. For various reasons it is aimed to have all the furnaces on the same ore-mixture. To this smelting charge he adds the profit that he ought to make to obtain a proper interest on his investment, allowing for the necessary amortisation of his outlay in plant. The further addition of the freight on the ore to his works, and on the spelter product to its market, with allowances for the expenses incurred in buying the ore and selling the spelter, gives the returning charge which he must make against the ore in buying it on the basis of f.o.b. (free on board at port of shipment) or f.o.r. (free on rail) at the mine or concentrating mill where produced.

Within recent years a marked change has taken place in the quality of the ores supplied to the zinc smelter. As the result of the gradual exhaustion of the high-grade calamine supplies, and even of the richer blende ores, and also the increasing demand for zinc, sulphide ores are now readily purchased which earlier would have found a poor market. It is not long since 50 per cent. of zinc in a blende product was a standard which admitted of little reduction, particularly amongst smelters in this country.

For several years prior to the war, however, it was possible to market ore containing only 35 per cent. of zinc, but as the price of spelter has advanced considerably since the outbreak of war, many smelters have refused to buy ores carrying less than 40 per cent. of zinc, in order to secure as large an output of metal as possible from their furnaces. As a general rule, zinc smelters consider low-grade ores only if they contain other metals, such as lead and silver, in sufficient amounts to render the residues, after extraction of the zinc, profitable commercial sources of those metals, and thus to recoup the loss due to the decreased zinc content of the ore. Such foreign metals are, however, naturally paid for at a low price owing to the incompleteness of their recovery.

That these secondary sources of profit may nevertheless become substantial is shown by the fact that, whereas zinc concentrates were formerly subject to a deduction or "penalty" by the smelter for shortage of zinc below a certain figure, and the ore producer, therefore, did his best to increase the zinc tenor and to decrease that of lead and silver, he is now subject to a penalty if the zinc content is above a certain limit when this involves what the smelters consider to be an undue absence of silver or lead in connection with a given smelting charge. This applies more particularly to the Broken Hill and similar zinc concentrates. These zinc blende concentrates contain a payable quantity of silver, to recover which a certain amount of lead must be present. Thus the Continental smelters, who formerly treated large quantities of the Broken Hill concentrate, called for a product containing not less than 8 per cent. of lead, which metal they required for collecting the silver when smelting the residues, although the flotation process is capable of producing a zinc concentrate much lower in lead if desired.

### The European Ore Trade

Owing to the growing shortage of the supply of domestic zinc ores and the ever increasing demand for zinc during the past 30 years, the European smelters have had to rely more and more on imported ores, and this resulted in a European ore trade that, at the outbreak of the war, had grown to considerable dimensions.

For many years, large quantities of zinc ore have been shipped to Antwerp and to Swansea from Sardinia, Algeria, and Spain, and also in more recent years from Australia and America. Despite the growing disposition of the American smelters to adapt their works to the handling of all classes of ores, the shipment of zinc ores from America to Europe has in the past been important, and the tendency before the war appeared to be for the shipments to increase rather than to decline. The American ore was shipped from Colorado via the Gulf ports of Galveston and New Orleans, cheap ocean freights being secured on the steamers carrying cotton to Europe.

The ores were shipped to Antwerp and to Swansea in bulk, as no sacks appear to be proof against the acid nature of the ore. The ore arrived in the condition of fines, having generally been calcined, if calamine, and roasted, if blende, except in the case of Australian concentrates.

The cargo was sampled by reserving one basket in twenty-five during unloading, the sample basket being chosen at random by agreement between the representatives of the buyer and seller, or, more commonly, the agent to whom both parties had entrusted their interests in this part of the business. The ore reserved for sample was reduced in quantity either by machinery or mixed and quartered down by hand to obtain a small representative quantity for assay to determine the zinc content and the presence of objectionable impurities.

Settlements were made in Antwerp and Swansea on the results of the assay. The ores were bought on different formulæ, of which an example has been given on p. 75.

The formula quoted was used for ores containing 46 per cent. of zinc or more, and was quoted only on consignments c.i.f. Antwerp (costs, insurance, and freight paid to Antwerp).

As already stated, this formula is based on payment for the metallic content of the ore, less 8 units, 95 per cent. of the London price of spelter, G.O.B., less a returning charge.

The following approximate figures, making a total of nearly 900,000 tons, show the extent of the European ore trade in 1913:---

Zinc ore imported i	English tons, 2,240 lb.				
Germany	• •			••	308,000
Austria-Hungar	y	• •	••	••	50,000
Belgium	••	••	••	••	300,000
France	••	••	••	••	173,000
United Kingdon	a	••	••	••	65,000

To what extent the European zinc ore trade will be resumed after the war is very difficult to predict.

### CHAPTER V

#### THE SMELTING OF ZINC ORES

PRACTICALLY the whole of the world's supply of zinc is obtained by the distillation method in retorts in which advantage is taken of the volatility of the metal at a bright red heat. Until quite recent years this was the only method of zinc production, but at the present time appreciable and increasing amounts of the metal are being produced by wet processes, and by electrothermic smelting.

Preliminary Treatment.—For the distillation method the first clearly-defined stage is the conversion of the zinc compounds present in the ore into oxide by calcination or by roasting, and this is followed by the reduction of the oxide to metal by means of carbon at a temperature which is higher than the boiling point of zinc, *i.e.*, about 940° C. (Moissan).

These two operations are so distinct that they may be, and often are, carried out for commercial reasons in establishments widely distant from one another.

The processes of calcination and roasting are different in their operation, but both aim at the same type of product, *i.e.*, zinc oxide that is reducible under the conditions of distillation.

*Calcination*.—Calcination is used for the expulsion of carbon dioxide and water from carbonate ores, and of water from hemimorphite; it also renders the ore more porous, and therefore more readily acted upon by the carbonaceous matter employed for its reduction.

Although it is possible to reduce zinc carbonate without previous treatment, this practice is seldom adopted, as it has been found more economical to calcine the ore first. Apart from any other reason, the economy in freightage between mine and smelter, as previously stated, is usually sufficient to warrant calcination, the saving thus effected being of increasing importance the more widely apart the two are situated.

Calcination is a simple operation, and analogous to the burning of limestone for lime, being carried out in practically the same manner, usually in kilns, in the presence of excess of air and also of moisture, the two latter points being important for the attainment of a good product.

The use of kilns is restricted to lump ore, or to a mixture of lump and fines, usually in alternate layers, whereas for finely crushed ore furnaces either of the reverberatory type, or revolving cylindrical furnaces with a continuous discharge, of the Oxland type, are used.

The method of calcination employed in Sardinia, where some of the most important deposits of calamine exist, may be taken as typical of the best practice in Europe. The lump ore is charged into slightly conical, circular shaft furnaces, 6.5 ft. in diameter at the bottom and varying from 12 to 18 ft. in height. The heat is supplied either from external grates, or by charging the furnace with alternate layers of coal and ore. The former method is preferable, as it avoids the contamination of the ore with ash from the fuel. The complete dehydration of the hydrated zinc minerals is readily effected by heating to the dullest perceptible red heat, but when other carbonates are present a higher temperature is necessary.

The chief carbonates associated with calamine and the approximate temperatures required for the expulsion of their carbon dioxide are as follows<sup>1</sup>:---

Zinc carbonate				300° C.
Magnesium carbona	te	••	••	650° C.
Iron carbonate		••		800° C.
Calcium carbonate	••	••	•••	812° C.

Owing to the comparatively high temperature required to decompose calcium carbonate, calamine ores containing a high proportion of this carbonate are the most difficult to calcine completely, and they usually retain a sensible proportion of their original carbon dioxide content.

The calcination of calamine is seldom complete, and when the ores are contaminated with much calcium carbonate or magnesium carbonate as much as 15 per cent. of carbon dioxide may be retained.

<sup>1</sup> Ingalls, "Metallurgy of Zinc."

*Roasting.*—The desulphurisation of zinc blende is a more difficult matter than the process of calcination as described above.

It is usually effected on the crushed ore by roasting in the presence of an excess of air, in shelf furnaces of two or more shelves. The particles of ore should not exceed 2 millimetres in diameter. Numerous difficulties are encountered in the process, which requires considerable experience on the part of the man supervising the work. Especially is care necessary to transform the sulphide as completely as possible into oxide and at the same time to avoid its passage into the sulphate, as the latter is reduced to sulphide by carbon, instead of to the metal.

Of all the metallic sulphides with which the metallurgist has to deal, zinc sulphide is one of the most troublesome to roast "sweet," *i.e.*, to expel all the sulphur.

It has, however, the advantage of not sintering by heat, so that in the process of roasting it may from the first be exposed to a higher temperature than most other metallic sulphides. The roasting is considerably complicated by the presence of other metallic sulphides, such as those of iron and lead, and by the presence of manganese, lime, strontia and barytes. The first effect of the elevation of the temperature in roasting is to distil off sulphur, reducing the sulphides to a lower stage of sulphurisation. This sulphur burns in the furnace to sulphur dioxide (sulphurous anhydride, SO<sub>3</sub>) part of which coming into contact with the hot ore and hot walls of the furnace, and the oxidising furnace gases, is converted into sulphur trioxide (sulphuric anhydride, SO<sub>2</sub>). On raising the temperature the decomposition of zinc sulphate and other metallic sulphates is effected, leaving oxide of zinc contaminated with the oxides of other metals present. For the expulsion of the sulphur trioxide from the zinc sulphate, however, a very high temperature is required, especially from the basic sulphates, which remain towards the end of the process, and it is this fact which makes the perfect roasting of zinc blende difficult.

The oxidation of both the zinc and the sulphur in zinc blende by atmospheric oxygen during the roasting operation may be represented by the following equations:—

$$ZnS + 3O = ZnO + SO_2.$$
  

$$2ZnS + 7O = ZnO + ZnSO_4 + SO_2.$$
  
At a higher temperature, 
$$ZnSO_4 = ZnO + SO_3.$$
  
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The reactions in blende roasting being exothermic, the ore, when once sufficiently heated, is self-roasting until the total sulphur contents are reduced to about 8 per cent. Beyond this stage the further application of heat becomes necessary in order to decompose the sulphates, so that the final reactions are strongly endothermic, and the temperature of the ore when roasting is complete is about 900° to 950° C. The amount of sulphur to be expelled is dependent on the amount of metallic sulphides associated with the blende. Pure zinc sulphide contains 32.92 per cent. of sulphur, but the ores of commerce are usually contaminated with iron pyrites (FeS<sub>2</sub>) and other metallic sulphides and gangue materials, so that the sulphur content is usually between 21 and 35 per cent.

When roasting has been successfully conducted, the final product does not contain on the average more than I per cent. of sulphur. Thus, in the case of certain of the purer ores the desulphurisation is so complete that no more than 0.5 to 0.8per cent. total sulphur remains, whilst others equally carefully dealt with retain from 2.5 to 3 per cent., and even more in special cases, particularly those ores containing lime and baryta. Following modern Continental practice, however, the sulphur combined with lime, magnesia, strontia and baryta should be considered separately from that otherwise present in the roasted ore.

The loss of zinc in roasting is very small and averages only about 0.5 per cent. Probably highly ferruginous blende is the most difficult ore to roast.

Zinc ores are rarely absolutely free from lead, and the trouble introduced in the operations of roasting and distillation by the presence of this metal in substantial amounts prevented to a large extent the smelting of zinc-lead ores until about 1890, when they were first smelted on a large scale on the Continent.

Broken Hill ore, containing from 17 to 33 per cent. of lead and from 28 to 34 per cent. of zinc, was treated in Belgium and Germany in 1897, the ore being roasted in hand furnaces and the zinc distilled, after which the residues were treated for the silver and lead.

Zinc concentrates from the dressing of the Broken Hill ore were first shipped to the Continent in 1899, and contained from 12 to 15 per cent. of lead and from 38 to 40 per cent. of zinc. They were first smelted in Belgium and Holland and a little later in Germany. The treatment of Broken Hill concentrates in this country was first commenced in 1905 by Mr. H. M. Ridge, who in 1907–1908 built and started the works at Seaton Carew, Durham, where large quantities of this ore are now treated.

Roasting converts lead sulphide (galena) into lead oxide, and to lead sulphate, a stable compound very difficult to decompose even at a high temperature. In the presence of free silica lead silicate is formed, and since this compound is readily fusible there is a risk of the ore agglomerating during roasting if it contains much quartz. Considerable success has attended the attempts to roast zinc-lead ores, and now excellent desulphurisation of Broken Hill concentrates, containing about 45 per cent. of zinc and as much as 10 per cent. or more of lead, is daily achieved by well-designed muffle roasting furnaces.

It has been found in practice that the rhodonite (mainly manganese silicate) which is mechanically mixed with the zinc ore in Broken Hill concentrates has a peculiar beneficent effect in the roasting, but the reasons for this are not clear, and the matter requires investigation.

The reactions peculiar to the roasting of Broken Hill concentrates appear to reach their maximum effect in muffle roasters, and are not nearly so noticeable when the roasting is carried out in furnaces of the "open" type.<sup>1</sup> In fact it may be said that the successful treatment of zinc-lead ores is due largely to the improvements in the design of modern roasting furnaces of the muffle type.

The surmounting of the difficulties which at first attended the roasting and subsequent distilling of the Broken Hill and similar zinc concentrates is a matter of far-reaching importance, as it renders available vast additional sources of ore for augmenting the world's supply of zinc.

Many types of furnaces are in use for roasting zinc blende ; they may be classified under four heads, viz. :---

(1) Hand-raked reverberatory furnaces with one or more hearths, or with shelf burners.

(2) Mechanically-raked reverberatory furnaces.

(3) Multiple-hearth hand-raked furnaces.

(4) Mechanical multiple-hearth muffle furnaces.

The work of stirring in zinc ore-roasting furnaces is most

<sup>1</sup> J. C. Moulden, op. cit., p. 508.

#### THE ZINC INDUSTRY

laborious, and even on the Continent, where labour is comparatively cheap, continuous efforts have been made, since the beginning of the industry, to replace hand labour by machinery. The first attempt was made by the Société de la Vieille Montagne, who succeeded in carrying out the first part of the operation in a circular furnace with several hearths, 8 feet in diameter, in which the ore was stirred by means of rotating rabbles. The ore, after passing over three or, in some of the furnaces, four hearths, dropped to two hand-rabbled hearths similar to those used in the Rhenania furnaces described later. In America, where hand labour was even more difficult to obtain, it was impossible to use hand furnaces.

Roasting furnaces of the muffle type are employed when it is desired to utilise the sulphur dioxide for the manufacture of sulphuric acid, as the fuel gases never come into direct contact with the ore, the sulphur gases from which are led by an independent flue system to the sulphuric acid plant. The gases that pass to the acid maker contain on an average between  $5\cdot5$  per cent. and  $6\cdot5$  per cent. (by volume) of sulphur dioxide. If below 5 per cent., the acid-chamber reactions are retarded, while if sensibly above 8 per cent. the roasting is retarded.

Further reference is made to the manufacture of sulphuric acid from blende roasting on page 111.

The utilisation of the sulphur contents of zinc ore has received considerable attention within recent years on the Continent and in America, with the result that furnaces of the muffle type, either hand or mechanically raked, are now largely employed for roasting blende.

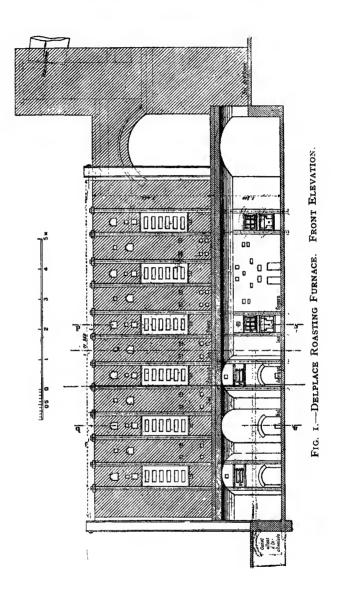
Representative furnaces of this type now in use are (I) the Hasenclever or Rhenania furnace, (2) the Delplace furnace. (3) the Hegeler furnace, and (4) the Ridge furnace.

The first two named are hand-worked muffle furnaces and are almost exclusively used in Europe; and the third is a mechanical furnace in general use in the United States. Hasenclever built his first furnace at the Rhenania Works in Germany in 1855, and since that time many modifications have been introduced. In the later modifications, the Rhenania furnace consists of three superimposed muffles, the fire gases travelling beneath and above the bottom muffle.

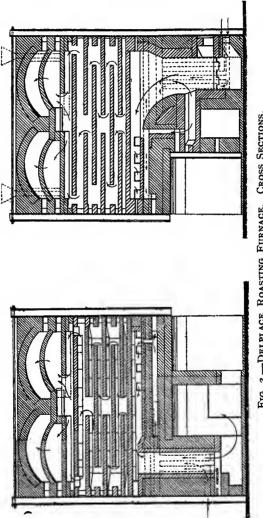
The furnace is 47.5 ft. long and 17.5 ft. wide, so that the ore travels a distance of 118 ft. along the hearths. With a 12-hour

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THE SMELTING OF ZINC ORES



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shift a total of 8 men is required for the production of 6 tons of roasted ore per 24 hours.<sup>1</sup>

By working with 8-hour shifts only 12 men were required, and the production per man per shift slightly decreased.

The coal consumption is about 25 per cent.

These furnaces have been generally built together in blocks of four and have been more largely used on the Continent than any other type of furnace.

Owing to the high price of fuel, "Delplace" furnaces have, since 1895, been largely built in Belgium. Figures 1 and 2 show the details of this furnace.

The travel of the ore on the seven superimposed hearths in this furnace is only 40 ft., but the ore is exposed thoroughly to the air because the arches are low, and only a thin bed of ore is maintained on each hearth. Only 16 per cent. of coal is required for heating. It is stated that with good labour, and if carefully built, these furnaces give satisfactory results. In addition to those erected in Belgium, some have been built in France, and a few have been erected in this country and in Germany.

Experienced labour is required to work them satisfactorily, and the men prefer to work on the Rhenania furnaces, in which the ore is rabbled sideways, instead of being alternately pushed from and drawn towards the worker as in the Delplace furnace.

As previously stated, work on zinc ore-roasting furnaces is most laborious, and continuous efforts have been made to replace hand labour by machinery, especially in furnaces in which the gases are used for sulphuric acid production. The mechanical operation of the muffle furnace, however, presents considerable difficulty, and although much progress has been made in recent years, it does not appear to have reached the development and application which every zinc metallurgist hopes it may do.

The Hegeler furnace, so largely used in America, is a mechanically worked multiple-muffle furnace, in which seven muffles are placed one above the other, two furnaces being built to form one block. Figures 3 and 4 illustrate the general design of the Hegeler furnace.

The three lowest muffles are heated by producer gas, the flame passing first under and then over them. The ore is rabbled mechanically by rakes attached to iron rods, so that it travels

<sup>&</sup>lt;sup>1</sup> "The Utilisation of the Sulphur Contents of Zinc Ore," H. M. Ridge, Journal of the Society of Chemical Industry, 1917, vol. xxxvi, pp. 676-685.

from shelf to shelf, finally being discharged through an opening in the lowest shelf. The rakes are drawn through the furnace by chains, and after passing through the furnace in one direction are moved to the level of the next shelf, and then drawn through this in the opposite direction. This allows of cooling the stirring mechanism whilst outside the furnace.

These furnaces occupy a very large floor area, and the capital

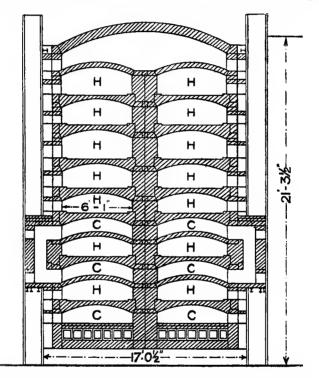


FIG. 3.—HEGELER ROASTING FURNACE. SECTIONAL ELEVATION. H=MUFFLES. C=GAS FLUES.

outlay is large. They have been adopted in America on account of the scarcity and dearness of skilled labour and because coal is cheap. It is stated that the repair bill of the Hegeler furnaces working on the Continent is such that there is no appreciable saving in cost of roasting as compared with hand-rabbled furnaces. With 8-hour shifts 17 men are required per shift, so that there is no reduction in the actual number of men as compared with hand furnaces, but, with the exception of a few mechanics, the men can be of the unskilled labour class.

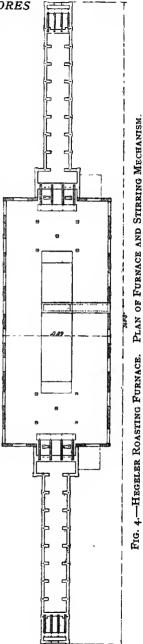
A 75-ft. furnace roasts 48 tons of ore to a sulphur content of 1.25 per cent. in 24 hours, with a consumption of coal of about 30 per cent. of the raw ore. The gases from the roasting contain 4.75 per cent. by volume of sulphur dioxide and are utilised for the manufacture of sulphuric acid.

The improvements in the Hegeler furnace since its introduction about thirty years ago have been only in structural features and mechanical details. Most of the new zincsmelting plants in the eastern coalfields of the United States are designed to make sulphuric acid, and are equipped with mammoth Hegeler furnaces capable of roasting about 50 tons of blende per day.

Another muffle furnace operated mechanically which is being experimented with in Europe, and to a certain extent in America, is the De Spirlet furnace, invented by a Belgian engineer of that name. This is a multiple-hearth turret furnace, in which the alternate hearths rotate and the ore is stirred by means of special bricks projecting downwards from the hearth above.

In consequence of there being no metal parts inside the furnace in contact with the ore, the fuel consumption is low. The capacity of the furnace is 3 to 3.5 tons per 24

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hours. Good results are stated to have been obtained, but the campaign is short, and as soon as one or two of the projecting bricks which stir the ore wear or break off, the furnace chokes and has to be cooled.

In this country several Merton roasting furnaces have been in use in South Wales for some years. This furnace, which is of the open-hearth reverberatory type, has three superposed hearths and a special finishing hearth, the ore being stirred by means of revolving iron rabbles attached to vertical shafts which pass through the top of the furnace and through all three hearths and are supported in sockets below the lowest hearth. There are four sets of rabbles for the main hearths, and one or sometimes two water-cooled rabbles for the finishing hearth. The motion of the rabbles gives a circular rabbling to the ore, and produces a slow forward movement of the ore owing to the paths of the rabbles slightly overlapping. The hearths are level and communicate with one another by short vertical channels. The crushed ore is fed in at the coolest part of the uppermost hearth, is gradually drawn by means of the rabbles along each hearth, and finally discharged through an opening in the finishing hearth into a truck below it. The necessary heat is supplied by a fire-place at the end of the finishing hearth near the discharge opening. The furnace in use at one of the Swansea works has four hearths 10 ft. wide, with four sets of rabbles. The finishing hearth is 6 feet wider than the others, and has two rabbles cooled by circulating water in the usual way.<sup>1</sup>

The latest type of mechanical-rabbled furnace used in this country for roasting zinc blende is the Ridge furnace illustrated in Figs. 5 and 6, which appears to be gaining favour.

It consists of three muffles placed one above the other, and is gas fired, the gas being burned only under the bottom muffle or hearth, experience having shown that it is not necessary, with proper design, to pass the fire gases both beneath and then above the bottom muffle as is frequently done. The general design of the furnace is shown in the illustrations. The ore is stirred by means of iron rabbles attached to four vertical iron shafts passing through all the roasting hearths and made to revolve by suitable mechanism beneath the furnace. The shafts are each made in one piece and are water-cooled; about 15,000 gallons of cooling water are passed through the shafts in

<sup>1</sup> Gowland, "Metallurgy of Non-ferrous Metals," London, 1914, p. 29.

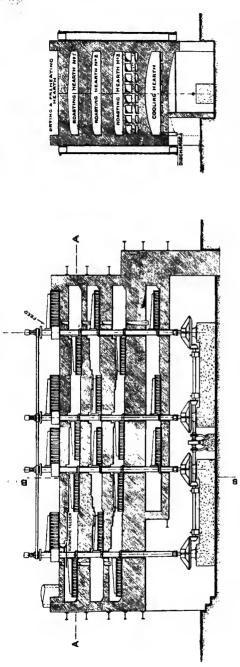
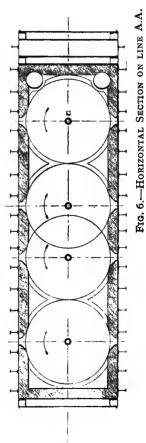


FIG. 5.-RIDGE ROASTING FURNACE. LONGITUDINAL SECTION.



CROSS SECTION ON LINE B.B.

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24 hours to prevent overheating. The rabbles which stir the ore are easily and quickly renewed and the part to be replaced weighs only 5 lb. The ore is fed continuously to the drying hearth on top of the furnace and passes over three roasting hearths and finally to the cooling hearth, where it serves to preheat the air required for the oxidation. The mechanism of each furnace is driven by a separate electric motor of from 8 to 10 horse-power. The motor and all the gearing are on a solid foundation beneath the furnace and fully accessible. The discharge opening is separated from the gearing by a brick wall to keep out all dust. The furnace runs noiselessly, the only sound being the hum of the motor. In this furnace Broken Hill zinc concentrates are roasted down to 0.75 per cent. total sulphur with a feed of 12 tons of ore per day of 24 hours and a coal consumption of 10 per cent. The sulphur fumes leave the furnace with  $6\frac{1}{2}$  to  $8\frac{1}{4}$  per cent. sulphur dioxide and at a temperature of 380° C. so that they can be used satisfactorily for sulphuric acid production in the lead chamber process. One man per shift can attend to the furnace and the producer.

Zinc concentrates with 14 per cent. lead have been satisfactorily treated, and also concentrates with 17 per cent. iron ; when roasting an ore, high in lead or iron, it is essential that a mechanical furnace be kept working continuously, because half an hour's stoppage means that the ore on the hearths sets hard and forms lumps which have to be broken up. It has been found possible in this furnace to use the rabbles for breaking up the lumps, and the gearing can, if necessary, be run alternately backwards and forwards till the hearths are free.

Reduction and Distillation.—The extraction of the zinc from the calcined or roasted ore is effected by mixing it with crushed coal or coke and exposing it to a high temperature in fire-clay vessels or retorts so as to reduce the zinc oxide. The carbonaceous matter must be in excess to prevent the formation of carbon dioxide, which acts as an oxidising agent on zinc vapour, in which condition the reduced metal is obtained.

The vapour distils off and is condensed to liquid metal in clay receivers attached to the retorts, and a continuous stream of carbon monoxide issues from the retorts.

Owing to the chemical and physical characteristics of the metal, the extraction of zinc from its oxide by distillation is by no means as simple as the reduction of most other metallic oxides. The reaction between zinc oxide and carbon is highly endothermic, and cannot therefore take place without external heat. Whether, and to what extent, zinc oxide is reduced by carbon monoxide is still a question of much controversy. The oxide is not sensibly reduced by carbon below a temperature of 1125° C., and in modern practice the retorts require to be heated to 1400° C. to effect the reduction. At this temperature the reduced metal is in the condition of vapour, and is not only extraordinarily susceptible to ordinary oxidising influences, such as air and water vapour, but is capable even of being oxidised by carbon dioxide. In ordinary distillation practice so small an amount as 0.25 per cent. of carbon dioxide in the retort is quite inadmissible, hence the great importance of keeping excess of carbon in the retorts.

Under these conditions the condensation of the zinc vapour to liquid metal is a matter of considerable difficulty, as it can only be effected within a limited range of temperature, viz., between 415° and 550° C. Below 415° C. it condenses to a powder called zinc fume or powder, which consists of finely divided metallic zinc mixed with zinc oxide to the extent of 6 to 10 per cent. If the temperature is much above 550° C. the vapour is not condensed at all.

Another difficulty also attends the condensation. If the zinc vapour is much diluted with other gases, it will not condense to fluid zinc, but only as zinc fume.

The facility with which zinc oxide is reduced is also affected by the temperature at which it has been produced in the preliminary roasting of the ore. The oxide obtained by roasting zinc blende requires a higher temperature for reduction than that from the calcination of the carbonate. Also, the higher the temperature at which zinc blende has been roasted, the higher is the temperature required for the reduction of the resulting oxide.

According to W. McA. Johnson,<sup>1</sup> pure zinc oxide is reduced by charcoal at  $1022^{\circ}$  C., and by soft coke at  $1029^{\circ}$  C. When, however, the zinc oxide is roasted at  $1100^{\circ}$  C., reduction with soft coke only takes place at  $1048^{\circ}$  C., and on roasting the zinc oxide at a temperature of  $1300^{\circ}$  C., reduction is not effected until a temperature of  $1061^{\circ}$  C. is reached. In actual practice

<sup>1</sup> American Electrochemical Society, see *Electrochemical Industry Journal*, 1904, ii, pp. 185–187. it does not appear to be an invariable rule that the reduction temperature is dependent on the temperature at which the zinc oxide has been produced, and further investigation on this point appears to be necessary.

It is customary among smelters of other metals to speak of the metallurgy of zinc as behindhand and lacking in the care and completeness which characterise their own practice. When, however, the inherent difficulties attached to the art of extracting zinc, as outlined above, are appraised at their proper value, this reproach is unmerited. Much as it leaves to be desired, the modern metallurgy of zinc is not substantially inferior in its methods and practice to that of the other metals in common use. The difficult and peculiar conditions attending the reduction and distillation of zinc render it necessary to adopt special methods of extraction, since owing to these conditions the metal cannot be extracted in large quantities in blast or reverberatory furnaces, as is the common practice with other industrial metals. In zinc extraction the ore charges, which are necessarily kept in the condition of coarse powder throughout the operation, are very poor conductors of heat, and to extract the metal it is necessary to supply heat energy continually by external heating of the retorts. This imposes a maximum charge thickness of about 8 in., a 24 hours' reduction period (from charging to recharging), the provision of small-sized retorts of specialised construction, and with only about six weeks' life, and generally the handling of large bulks of raw material in very small quantities. Also, it does not pay to carry the extraction of the zinc below a certain limit, consequently the residues are dumped when still carrying several units of zinc. Nevertheless, viewing the present status of the practice in zinc smelting, one cannot but be impressed by the high extraction results, the low consumption of fuel made possible by modern methods of gaseous firing and the reduction of labour involved in the process.

The methods of distillation now in use may be conveniently classified into (I) Belgian, (2) Silesian and (3) Rhenish or Belgo-Silesian. The chief differences in these methods are in the shape, size and arrangement of the retorts in the furnace.

The retorts in the Belgian process are circular or slightly elliptical in cross section, about 8 in. in diameter, 4 to  $4\frac{1}{2}$  ft. average length and arranged in the furnace in from two to seven rows.

In the Silesian process there is, as a rule, one row of large, narrow, muffle-shaped retorts to each furnace, although occasionally two rows are used. On an average the retorts are  $5\frac{1}{2}$  ft. long,  $2\frac{1}{2}$  ft. high and 6 to 8 in. in breadth. The Rhenish process employs retorts somewhat larger than those used in the Silesian process; they are muffle-shaped or elliptical, and arranged in two or three rows. This type is a combination of the best features of the Belgian and Silesian types, and is the one now very generally adopted in erecting new plant. The retorts are about 5 ft. long, 13 in. high and 6 in. wide. A modern type of Rhenish retort is shown in Fig. 7.

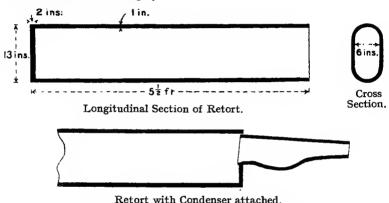


FIG. 7.—RHENISH RETORT FOR ZINC DISTILLATION. SECTION.

The Belgian and Silesian furnaces formerly in extensive use are being replaced on the Continent and in England by the Rhenish type of furnace. The Belgian type of furnace is however, still in use in the United States, although here also in the more recently erected plants the furnaces have been so modified that they may be classified as Rhenish. The type of retort used in the United States is practically the same for all plants. The length of the retorts varies from 4 ft. to 4.5 ft. in length, according to the size of the furnace, with a circular interior of from 7.5 to 8.5 in. in diameter.

To the mouth of each retort is luted a simple fire-clay nozzle or condenser, in which the zinc accumulates, and again fitted over the mouth of the condenser is a conical sheet-iron tube or prolong, which serves to condense and collect the "fume" which passes over along with the zinc during the distillation, and which is detached by the workmen and returned to the retorts with a subsequent charge. The condensers vary in form according to the retort capacity, type of furnace and system of distillation. They may be plain clay cones, conical-bellied to act as a metal receptacle, or  $\mathbf{\Omega}$ -shaped. They are made of less refractory clay than the retorts, and are sometimes coated with limewash, to facilitate the removal of adherent material.

Manufacture of Retorts and Condensers.—The manufacture of retorts and condensers is always carried out in close proximity to the smelting works, and forms a most important branch of the art of zinc extraction, since owing to the nature of the process of distillation there is a constant destruction of retorts, their life in modern practice being usually from forty to forty-five days.

The retorts were formerly made by hand, but in modern practice they are shaped by means of a hydraulic press capable of making 250 in a nine-hour shift. Machine-made retorts are greatly superior to those made by hand, as they are denser and on this account more durable and less permeable by zinc vapour. The material used for the manufacture of the retorts must be extremely refractory, and considerable difficulty is frequently experienced in obtaining clay suitable for the purpose. The raw clay needs careful weathering and pugging before use. Usually retorts are made of a mixture composed of burnt clay, or chamotte and sufficient raw clay to act as an efficient binding agent. In modern practice, finely-divided coke is often used to replace part of the chamotte, as it assists in retaining the shape of the retort under great heat and gives density and impermeability.

A typical retort mixture would consist of <sup>1</sup>:

Crushed burnt clay	(chamo	otte)	••	••	50 p	arts.
	••	••	••	••	40	.,
Finely-ground coke	••	••	••	••	10	

The retorts are dried very gradually by standing upright in rows in chambers heated to a moderate temperature, and before being placed in the distillation furnace they are tempered by gradually heating in kilns until they attain a full red, in which condition they are transferred to the furnace and luted in position. An old zinc retort shows a great alteration of texture, zinc oxide reacting with the alumina of the clay to form zinc spinel,  $ZnO.Al_2O_3$ , silica being liberated.

In modern plants, the condensers are moulded by means of a machine capable of producing from 1,000 to 1,200 per shift of nine hours. The mixture used consists of crushed old retorts and raw clay, and after leaving the moulding machine they are carefully dried and burnt before use.

The question of refractories for use in connection with zinc furnaces has recently received considerable attention, and the Ceramic Society has appointed a sub-committee to prepare a report on the subject.

A modern distillation furnace consists of an arched chamber containing a large number of retorts arranged nearly horizontally in two or three superimposed rows, one above another, and supported only at both ends in order that they may be surrounded by flame. Usually the retorts are arranged in two sets, back to back, with an intervening space for the gas and airports, the furnace being heated by producer-gas firing. The substructure of the furnace is usually arranged for preheating the air, or the air and the producer-gas, by a transference of heat from the waste gases of the furnace. Formerly reversing regenerative furnaces on the Siemens system were used, but in recent years counter-current recuperative furnaces have come into favour. The laboratory part of a zinc furnace, with retorts, without condensers attached, is shown in Figs. 8 and 9.

The older zinc furnaces were direct-fired by coal, but all modern furnaces are gas-fired. This results in economy in labour, fuel and repairs. The gas producers are built either in, or near, the furnaces, or in some cases entirely independent of them.

The ordinary life of a zinc furnace is about six years, but some regenerative furnaces have given good results even after eight to ten years.<sup>1</sup>

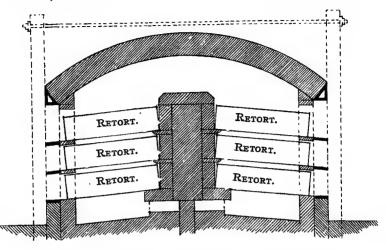
The zinc furnaces on the Continent hold from 100 to 240 retorts; the weight charged per retort is, according to its size, from 35 to 50 kg. of ore, plus 40 per cent. reduction coal, or a total of 47 to 70 kg., with 17 to 25 kg. of zinc.

The zinc dust produced varies, with the character of furnace and ore, between 4 and 10 per cent. of the spelter produced. The loss in metal varies between 10 and 15 per cent. according to the class of furnace and quality of ore. The durability of the retorts

<sup>1</sup> J. Gilbert, Mining Journal (London), 1916, vol. cxiv, p. 496.

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varies from thirty to forty-two days or more with three tier furnaces; that of the tubes varies between eight and twelve



JIC. 8.-ZINC DISTILLATION FURNACE. CROSS SECTION.

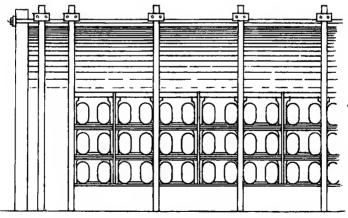


FIG. 9.-ZINC DISTILLATION FURNACE. FRONT ELEVATION.

days. The cost of retorts of 1,800 mm. length is about 4s., and that of the tubes from 5d. to 6d. each.

The German zinc smelters have closely watched the developments in gaseous firing, and in recent years the furnaces of the regenerative type have been replaced by counter-current or recuperative furnaces. This development was being carried out very quickly in Silesia in the last two years before the war in consequence of the rapid increase in the price of coal, which made it imperative for the smelters to economise in fuel. By replacing the regenerative furnaces by counter-current recuperative furnaces the German smelters reduced their fuel consumption appreciably and got higher extraction results in the distillation. The type of furnace which is in most general use in this country is the reversible regenerative gas-fired, but some of the newer plants have recuperative furnaces.

In America, natural gas has been extensively used for heating furnaces, and has become a very important distillation factor in the economic production of zinc in that country. The utilisation of these natural gas resources has permitted of the establishment of zinc distilleries in districts which otherwise offer no special advantage, the capital required and the working costs being so lowered thereby as to offset any disability attaching to transport of ore, clavs, reducing material and finished product.1

The process of distillation is not continuous, but consists of a well-defined cycle of operations repeated every twenty-four hours

The reduction of the zinc oxide in the roasted ore is effected by mixing it with about 40 per cent. of its weight of reducing material, in the form of coke, coal or anthracite. This proportion is about 21 times the quantity of reducing material required theoretically, but it is necessary in order to maintain a reducing atmosphere in the retorts, which is of vital importance for the reasons already stated.

As an example of the method of working, a brief account of the smelting of Broken Hill concentrates at the Port Pirie works, New South Wales, may be given.<sup>2</sup> The distillation plant com-prises 10 furnaces of the Rhenish type, having two tiers of retorts, back to back, with three rows of 24 retorts in each tier, i.e., 1,440 retorts in all. The retorts are elliptical in cross-section, and measure  $5\frac{1}{2}$  ft. in length and  $13\frac{1}{2}$  in. in height. The heating is effected by means of producer-gas, the air required for combustion being pre-heated by a counter-current system. The burners

<sup>2</sup> Bulletin of the Imperial Institute, 1916, vol. xiv, p. 65. 99

<sup>&</sup>lt;sup>1</sup> Moulden, loc. cit. p. 510.

are of the Bunsen type, 18 in. in diameter, with a gas inlet of 9 in. set in the hearth of the furnace between the two tiers of retorts. Each row of 24 retorts requires the attention of one man. The charge consists of about 10,000 lb. of roasted ore concentrates, 3,000 lb. of coke, and 1,500 lb. of coal. This is thoroughly mixed on the furnace floor and fed into the retorts through the condensers.

Usually the top and middle rows of retorts receive this charge, but the lower row, which does not get so strongly heated as the others, is charged with coke and material scraped from the condensers during tapping, consisting of zinc oxide and waste zinc.

The ends of the condensers are next partly stopped by luting on to them cast-iron tiles which have an inner lining of fire-clay and a hole for the passage of the evolved gases. This hole has a small projecting collar, into which is fitted the small end of a conical "prolong." These iron prolongs serve to collect the zinc dust not retained by the condensers. The temperature of the retorts is slowly raised until it reaches 1325° to 1350° C. The workman judges of the progress of the operation by the colour of the flame or vapour which is evolved.

When the distillation is complete, the prolong is removed, and, on releasing the iron tile, the molten zinc flows out and is caught in an iron ladle. The condenser is next scraped to remove all zinc and dross. The residue in the retort is removed by pulling down counterbalanced sheet iron aprons in front of the furnace to screen the men from the heat, and raking through holes. The residues fall out and are deflected by the apron into trucks below, whence they are sent to the lead blast furnace for the recovery of the lead and silver they contain.

Damaged retorts are next located, and after these have been replaced charging is recommenced. The whole series of operations occupies twenty-four hours. The recovery of zinc as spelter and zinc dust is stated to amount to about 80 to 85 per cent. of the quantity present in the ore.

The zinc dust collected amounts to about 12 per cent. of the total zinc obtained and contains about 92 per cent. of metallic zinc. This is sometimes returned to the furnace for recovery as spelter. The spelter contains from 2 to 3 per cent. of lead and is refined by being melted in a reverberatory furnace.

In modern works large condensers are used and the metal is

tapped once only into a mechanical ladle running along the furnace front, but with the ordinary small condensers the metal is tapped three or four times during distillation, and hand ladles are used for conveying the molten metal to the ingot moulds. The formation of some zinc powder is inseparable from distillation, but the proportion varies according to the method of working and may be deliberately controlled by placing common salt or other haloid salt at the mouth of the retort or even in the condenser.

This method has been very successful and is the subject of a patent by H. W. Webster and J. C. Moulden (British Patent No. 26788, 1910). In Belgium, salt is added to the charge for the same purpose. The amount of zinc dust produced varies in Continental works from 4 to 10 per cent., according to the class of ore and furnace employed.

The exhausted residues drawn from the retorts in the case of clean ores are usually thrown away. The composition of the residues naturally depends on the composition of the ores treated, and with average ores they may be said to contain as a rule from 4 to 8 per cent. of zinc. Residues containing lead and silver constitute an important by-product in zinc smelting and have been considered on p. 118.

In European practice, the amount of metal extracted by the distillation process is very generally referred to in terms of the percentage calculated upon the metal content of the roasted ore, since the smelter generally buys roasted ore and has no knowledge of the zinc content of the original sulphide ore.

The extraction of the zinc under modern European methods is given in broad terms as between 80 and 90 per cent., calculated on the roasted ore contents.

Thus the loss of zinc during smelting is large in comparison with the losses sustained in the different metallurgical operations employed for the production of other industrial metals. The zinc losses are subject to wide variations, according to the grade of ore, the impurities present and the care exercised in working. In the treatment of high grade ore carrying from 45 to 50 per cent. of zinc, as smelted in the best operated plants in Europe and in America, the loss is between 10 and 15 per cent.

A very sensible proportion of the total amount of zinc extracted from the ore is derived from the treatment of by-products, consisting of crusts of metal and oxide chipped off the condensers, condenser scrapings, oxide and dross from the metal ladles, all of which are recharged into the retorts.

Refining of Crude Zinc.—When pure ores have been employed, the zinc obtained by the distillation process is generally sufficiently pure for industrial purposes, but to ensure uniformity of product as far as possible it was formerly usual to remelt it in large kettles and recast it. The metal is poured into open iron moulds so as to produce slabs or cakes about  $17\frac{1}{2}$  in. by  $8\frac{1}{2}$  in. by  $2\frac{1}{2}$  in., weighing from 45 to 50 lb., and bearing the name of the smelting company.

Metal containing impurities such as lead is first submitted to a refining process known as liquation. This consists in melting the impure metal in large reverberatory furnaces with sloping hearths, holding from 20 to 30 tons.

As the slabs melt the metal runs down and collects in the well, or sump, situated at one end of the furnace bed, where it is kept molten at as low a temperature as possible.

The bulk of the lead separates by gravity and accumulates at the bottom of the bath, while the zinc, largely freed from lead, forms an upper layer from which the metal is ladled and cast into slabs as it collects.

With the exercise of every care, however, it is seldom that by this means the amount of lead can, in ordinary practice, be reduced below 1.4 per cent.

Several methods have been proposed in recent years for eliminating the lead in zinc-lead concentrates during the distillation process. One of these in use at Irvine, on the Firth of Clyde, consists in placing a filter of carbon, fire-brick, or other crushed and porous material in the mouth of the ordinary retort. This filter retains the lead while the zinc vapour passes through and is condensed.

Both filters and dams are in use in America and are effective in reducing the lead and iron content of the zinc, but have no apparent influence on the cadmium. Their effect is shown in the figures on p. 103 which give the lead content for different tappings of zinc.<sup>1</sup>

Their use has also reduced the iron content of the zinc from 0.07 to 0.02 per cent. Dams, however, have not found favour in the works, as they tend to reduce the yield of spelter.

<sup>1</sup> "Zinc Refining," L. E. Wemple, American Institute of Mining Engineers, 1917.

### THE SMELTING OF ZINC ORES

		First draw of zinc.	Second draw of zinc.
		 Lead per cent.	Lead per cent.
Condenser without dam	 ••	 0-58	1.48
Condenser with dam	 ••	 0.28	0.30
Condenser without filter	 	 0.66	1.28
Condenser with filter	 	 0.14	0.12

Another method, devised by Sulman and Picard, consists in briquetting the material with bituminous coal and pitch, and distilling the briquettes in an ordinary distillation furnace, when the carbonaceous residue is found to retain most of the lead in the metallic state, and is suitable for lead smelting. In this process the filtration of the lead takes place in the pores of the briquette itself.

The highest grades of zinc have to be produced either by the distillation of pure ores, by the redistillation of commercial spelter, or by special methods, such as electrolytic separation. The redistillation of ordinary spelter is responsible for considerable quantities of the high-grade zinc on the market. It has been largely used in America, especially since the outbreak of war, large graphite retorts being used for the purpose. Redistillation has also been carried out in electric furnaces in Norway and Sweden and has been very successful. It seems probable that the electric furnace will find extended application for this purpose in the future.

According to Juretzka,<sup>1</sup> "electrically heated furnaces are much more advantageous for the redistillation of zinc than the ordinary gas-heated muffle furnaces, as the temperature can be closely adjusted. A central condensing system is more economical than muffles fitted with condensers, and enables the process to be carried out under reduced pressure. High-grade zinc containing 99.7 to 99.8 per cent. of zinc is obtained from refined metal containing lead 1.0 per cent. and iron 0.03 per cent. by distillation at low temperatures in electric furnaces. The yield of pure metal is from 70 to 75 per cent."

<sup>&</sup>lt;sup>1</sup> "Manufacture of Pure Spelter," F. Juretzka, Chem. Zeit., 1916, xl, pp. 885-886, 894-896. (Abstract, Journal of Society of Chemical Industry, 1916, xxxv, p. 1263.)

Redistillation is essentially a fractional distillation process, the more readily volatile zinc being distilled and condensed, leaving behind the lead and iron in the distillation vessel. When, however, much lead is present in the crude zinc, the separation of this metal is never complete by redistillation. The process still leaves more than 0.25 per cent. of lead in the redistilled metal, and cadmium when present is also carried over with the zinc.

The electrolytic process, where available, produces a higher grade of spelter from impure ores than does the distillation process; a large portion of these impurities in the ore, which by the distillation process would be carried into the spelter, is removed in the leaching of the ore and the purification of the zinc solution.

## Recent Advances in Zinc Smelting

Whilst progress has been made in the metallurgy of zinc of late years, it has not been characterised by any great change in method, or by the discovery of new principles, but rather by a continuous and steady improvement in detail, an increase in the productive capacity of the existing works, and by the installation of new plants. Nevertheless, the minor changes have been important, and have been directed mainly towards higher extraction results and the reduction of labour. Whilst several new processes of zinc extraction are being experimented with on a comparatively small scale, these are not yet sufficiently developed to determine their influence on the future methods of metallurgical treatment of zinc ores.

The principal changes in zinc smelting in recent years are in the method of firing, first by the introduction of gas producers and reversing regenerative furnaces, and then by the adoption of counter-current regenerative furnaces, the use of machine-made retorts, the increase in the size, shape and dimensions of retort, from the Belgian to the Rhenish type, the use of improved condensers, large ladles for tapping, refining the metal without remelting, and mechanical mixing and transport of materials.

By these means the cost of production has been reduced and the yield of metal increased.

In the old direct-fired furnaces the coal consumption was over two tons per ton of ore smelted, whereas in modern gas-fired Belgian furnaces the consumption of coal for fuel is about 1.6 tons per ton of ore smelted. For Rhenish gas-fired furnaces the average has been about  $1\cdot 1$  to  $1\cdot 2$  tons, but at present it is 1 ton of coal per ton of ore; much necessarily depends, however, on the quality of the coal. With a view to the reduction of the cost of labour, mechanical appliances for charging and cleaning the retorts have been introduced in several European works, and more recently in American works, but they have not yet come into general use.

The ore charged into the retorts generally contains about 45 to 50 per cent. of zinc. The weight of the charge varies with the size of the retorts, the Belgian retorts in the United States taking about 60 lb. plus a small quantity of by-products, exclusive of reduction material, whilst for Rhenish retorts in Europe it is from 85 to 110 lb. Although the Saeger charging machine is now in regular use at the works of the National Zinc Company at Bartlesville, Oklahoma,<sup>1</sup> where it was introduced in 1913, the common arrangement of the distillation furnaces in American works is unfavourable to the use of a charging machine, American practice being to set the furnaces in parallel, whereas in modern European practice they are commonly set in series, *i.e.*, in a single row, thus allowing more room for manipulation. Machine charging takes one hour, as compared with three hours for hand charging, and the ore is charged more densely, enabling 2,000 lb. more ore to be charged into each furnace.

Two difficulties, however, attend machine charging when applied to the excessively fine flotation concentrates now coming to the zinc smelters. This very fine ore sticks to the augers, necessitating frequent cleaning during charging, and also tends to "blow out" with considerable force, sometimes only twenty minutes after they have been charged.

The method of removing the residue from the retorts generally employed in Europe is to rake them by hand into a pit in front of the furnace; in America the common practice appears to be to use a long iron pipe, with water flowing from the end, which is pushed to the back of the hot retort, where the water is converted into steam by the heat, throwing the charge forward.

By this method a considerable amount of fine material is blown away, causing loss of any silver or lead contained in the residue.

A retort-discharging machine has recently been patented by J. J. Simmonds, of Iola, Kansas, which in the opinion of some

<sup>&</sup>lt;sup>1</sup> "Mineral Industry," 1915.

distinguished American zinc metallurgists has solved the problem of mechanically discharging retort residues. It is stated that the machine has been installed at three zinc-smelting works in America. It consists essentially of a truck carrying a series of bars, or plungers, with sprockets at each end of the bar, over which travels an endless chain of scrapers. The machine is run up facing a tier of retorts, into which the scrapers are introduced and set in motion, the mechanical arrangements being very ingenious. The scraper chains are sprayed with water to keep them cool.

Careful attention is also given in America to the gangue constituents of the ore and the composition of the ash from the reducing agent employed, with the view of reducing the amount of slagging in the retorts. Iron, lime and manganese are the most objectionable impurities. Few American smelters care to have more than  $2\frac{1}{2}$  per cent. of iron present, but in Europe 7 to 8 per cent. is allowed, whilst ore with even as much as 22 per cent. has been successfully smelted.

The utilisation of the unburnt coal in retort residues is another matter claiming the attention of American zinc smelters. The residues, which contain a good deal of unburnt coal, are screened, and all material over  $\frac{1}{4}$  in. in diameter is mixed with about 20 per cent. of fresh coal and used as fuel under steam boilers. So far this mixture has proved serviceable at the works of the Edgar Zinc Company, and ten boilers are now fired in this way.

In modern German and Belgian practice a 90 to 94 per cent. yield of spelter is constantly reached with roasted blende carrying 50 per cent. of zinc. In the Western States of America the yield from a 40 per cent. ore is stated to be about 75 to 80 per cent., but in the newest plants efforts have been made to bring the yield up to that in Continental works.

Before the outbreak of war the English zinc smelters could not claim equality with the better Continental practice, the yield in this country in the past having been generally nearer 85 per cent. Although progress has been made in British works during the past decade, and gas-fired furnaces have almost completely replaced the older Welsh-Belgian type, much remains to be done in the older works to bring British practice up to the level attained in several Continental centres. During the past four years, however, there has been a considerable advance in the methods of British zinc works, and wherever new plant has been erected it has been of modern type, and should be productive of results equal to those obtained on the Continent.

In the past many attempts have been made to use vertical retorts in the distillation process, with the view of reducing the labour of charging and discharging the retorts, which is the principal part of that required in distillation. Hitherto such attempts have not been successful, mainly owing to the charge hanging in the retorts and preventing the gases and zinc vapour from escaping properly. More recently, however, the question of vertical retorts has been taken up on the Continent, and as the result of experiment it is now claimed that the old difficulties The reduction of the charge has been have been overcome. made a continuous process by the employment of vertical retorts in the Roitzheim-Remy furnace installed at Hamborn in Westphalia. In this process, "continuous reduction is obtained by feeding the preheated charge of ore into the top of a vertical retort, and discharging the cooled residue mechanically from the bottom of a cast-iron cooling chamber.

"The retort is open, top and bottom, but is sealed from the atmosphere by the charge and ashes. The clay condenser is arranged perpendicularly to the retort in a niche suitably heated, the front end being connected to a tube leading to the ' prolong ' catching the zinc dust, and the escaping carbon monoxide is burnt to ascertain if uncondensed zinc is present, the gases being passed into the main chimney. The furnaces are heated by gaseous fuel on the regenerative principle, and require little attention beyond superintendence of the machinery and tapping of the zinc once in twenty-four hours. Zinc of 98.6 to 99.0 per cent. purity is obtained, and is fairly free from lead. Several advantages over the Rhenish smelting system are claimed for the process, including the reduction, by 40 per cent., of the labour required, the lessened consumption of refractory materials in muffles and condensers equal to about 45 per cent., and a saving in tools, machine work, heating coal and general costs. but against these economies must be set the greater use of power for driving the discharging machinery, pumping cooling water, etc.

"The net result is stated to be, in the production of 15,700 metric tons, a saving of about £20,000 (407,000 marks).

"There are also the advantages of increased extraction, smaller

mechanical losses of ore and metal, the furnaces have much less dead space, are easier to regulate and superintend, and the furnace room is free from fumes.

"The costs of installation of both systems, without the discharging machinery, are stated to be about the same, though the wear and tear on the parts of the machinery are so small that their ultimate cost is negligible." I

In commenting on this process, Mr. W. R. Ingalls,<sup>2</sup> a wellknown American authority on zinc smelting, states that it may be accepted from Hr. Liebig's description, given above, that the continuous smelting of zinc ore in a vertical retort is an accomplished fact, and the development of the Roitzheim-Remy furnace should be watched carefully.

In 1916 application was made by the Swansea Vale Spelter Company for the transfer of German patents relating to the smelting of zinc ore in vertical retorts, and the employment of machinery for scraping the lower part of the furnace, with the object of erecting vertical retorts in this country to test the feasibility of the process as a commercial method of zinc production.

With a view to economise fuel and labour, and to render the process of zinc production continuous, numerous attempts have been made to smelt zinc ores in the blast furnace. All such attempts have failed, however, owing to inability to control the percentage of carbon dioxide which so readily oxidises zinc vapour at a red heat.

The small size, confined character and presence of an excess of carbon in the charge are conditions which in the ordinary retort process result in the carbon dioxide being kept within the necessary limits.

In the blast furnace the zinc can be reduced and separated from the ore as vapour, but owing to the conditions of working the vaporised zinc, which has to travel by the same outlet as the waste furnace gases, is much diluted with carbon monoxide and nitrogen, and is oxidised by the carbon dioxide invariably present,

<sup>1</sup> "The Roitzheim-Remy Continuous Zinc Distillation Process," by M. Liebig, Metall und Erz, 1916, xiii, pp. 143–156; also Metallurgical and Chemical Engineer, New York, 1916, xiv, pp. 625–629. The abstract quoted is from the Journal of the Society of Chemical Industry, 1916, xxxv, p. 846.

<sup>2</sup> Engineering and Mining Journal, New York, 1916, cli, p. 623.

so that only zinc oxide is produced. Apart from the fact that the condensation of vaporised zinc can only be effected within a limited range of temperature, it has been found that the zinc can be oxidised by as little as 0.5 per cent. of carbon dioxide in the furnace gases or by water vapour.

By rapid cooling of the furnace gases and other methods, it has been found largely possible to overcome this oxidation, but so far the process does not appear to have been generally employed on a commercial scale.<sup>1</sup>

Attention has already been drawn to the zinciferous dust which collects in the flues of the blast furnaces in which iron and manganese ores containing small quantities of zinc have been smelted. The percentage of zinc in the ores is very small, and its recovery affords an interesting metallurgical example of how the treatment of an iron ore, valueless as such from the point of view of zinc, results in a by-product containing often as much as 75 per cent. of zinc and correspondingly valuable.<sup>2</sup> It is produced by many of the iron blast furnaces in this country and in Sweden, and in the works at New Jersey, in the United States of America. It is a most important by-product in smelting franklinite residues for ferro-manganese.

Blast furnace smelting also implies the production of a fluid slag that will flow readily from the furnace, a condition prohibiting any excess of carbonaceous material, and one that is difficult to attain in view of the tendency of zinc to pass into the slag and render it pasty unless a high temperature is attained. It has been shown, however, that this difficulty may be overcome.

In ordinary blast furnace practice a temperature of  $1400^{\circ}$  C. was once considered high; but now a temperature of  $1500^{\circ}$  C. and upwards is reported. The conditions for low zinc retention in the residuum are, according to W. R. Ingalls,<sup>8</sup> a high temperature and a highly calcareous slag. Slags of this nature containing less than I per cent. of zinc have been made.

The smelting of complex zinc-lead ores in the blast furnace in the ordinary way suffers from two main disadvantages; upon the one hand the ores contain too much lead for the ordinary distillation process of zinc extraction, and on the other they contain too much zinc for lead smelting, their reduction in the

- <sup>2</sup> J. C. Moulden, loc. cit. p. 501.
- <sup>3</sup> Experiments at McGill University, 1912.

<sup>&</sup>lt;sup>1</sup> Bulletin of the Imperial Institute, 1916, vol. xiv, p. 70.

blast furnace being hindered by the excess of zinc, which requires special amounts of flux, and thus is slagged off and lost unless the slag is specially treated to recover the zinc.

The recovery of zinc from slags containing large quantities of the metal has been carried out by H. Pape's process at several places on the Continent, notably at the Oker Smelting Works in the Lower Harz district, where it has been applied to the treatment of the various complex ores from the Rammelsberg deposits, the main varieties of which are lead ores with 9 per cent. of lead and 20 per cent. of zinc, and copper ores with from I to I5 per cent. of copper and I to 20 per cent. of zinc. The ores are first subjected to a sulphurising roast and leached to remove some of the zinc; the residual ore is then smelted with fluxes in the ordinary way in blast furnaces.

The slags, containing from 22 to 27 per cent. of zinc oxide, are crushed to 50 mesh, mixed with coke screenings, and the mixture made into briquettes by means of pitch. The briquettes are then raised to a high temperature in a continuous reverberatory furnace, where the zinc after volatilisation as metal is carried off as oxide by the flue gases. After dilution with cold air, the gases are passed through bag-house plant to collect the oxide. The better quality caught in the bags is sold as a pigment, the rest is sent to a local zinc works, where it is used for enriching poor zinc ores, in order that they may be treated by the Belgian process.

Under conditions of forced oxidation, such as in the blast furnace or blowing hearth, lead is as freely volatilised in the form of oxide as is zinc, a fact which has been utilised in Germany, where the blowing of oxidised low grade zinc-lead ores has been practised, bag-house plant being employed to collect the mixed oxide fume. This fume is then treated with sulphuric acid for the production of crystallised zinc sulphate, the residual lead sulphate being sold to the smelter.

## CHAPTER VI

## ZINC SMELTING (continued)

## By-products in the Smelting of Zinc

## Sulphuric Acid

Not the least important of the varied problems that present themselves in the extraction of zinc from its ores is the disposal of the sulphur dioxide resulting from the roasting of blende. Not only has this to be considered on the ground of health and the preservation of vegetation, but there is the further important economic consideration of utilising the sulphur gases for the manufacture of sulphuric acid, and thus securing a valuable product that is not only essential to chemical industry, but one that also plays an important part in many other industries.

As previously pointed out, where the manufacture of sulphuric acid is one of the objectives, certain conditions are imposed upon the roasting of blende, the most important of which is the conducting of the operation in muffle furnaces, as the sulphur fumes must not be contaminated and diluted with fire gases.

Most zinc ores are free from arsenic, consequently the sulphuric acid made from blende roasting usually commands a higher price than that made from iron pyrites, which almost invariably contains arsenic. On the other hand, zinc ores frequently contain fluorine, as calcium fluoride (fluor spar), which flotation and other concentrating methods have, unfortunately, not, up to the present, been able to separate effectively. Calcium fluoride is decomposed in the roasting furnace in the presence of silica and forms silicon fluoride, which is subsequently decomposed and causes the brickwork in the furnace to be appreciably attacked unless special precautions are adopted. When the sulphur dioxide from blende roasting is converted into strong sulphuric acid of  $60^{\circ}$  Bé,, the yield from I ton of 40 per cent. zinc blende amounts, on the average, to 80 to 90 per cent. Whilst the old-established English lead chamber method of sulphuric acid manufacture has to meet the increasing competition of the newer contact processes, these up to the present have found but little application in this country in connection with zinc ore roasting, although contact processes are in use in America and in Germany.

The lead chamber process, when working with hand-rabbled roasting furnaces, has to be carefully watched because of the irregular evolution of sulphur dioxide in consequence of intermittent rabbling of the ore. In Germany it has been usual to reduce this difficulty by arranging for the furnace hands working on the different furnaces to start their shifts at different times, but, in spite of this, it is not possible to obtain a continuous current of uniform gas throughout the twenty-four hours, and, unless the process is watched carefully, loss of nitre will result.<sup>1</sup>

With modern mechanical furnaces this difficulty is completely overcome. Apart from some increase in the manufacture of sulphuric acid from blende roasting, there has been a large increase in the operation of contact plants for sulphuric acid production in this country since the outbreak of war, both as regards extension of existing works and the erection of new ones. Acid production was considerably increased in 1915 and 1916, and further small increase is in prospect. The importance of contact processes is therefore claiming the attention of British sulphuric acid manufacturers.

The contact process consists essentially in bringing about the combination of sulphur dioxide and oxygen by contact with heated finely divided platinum (hence the name "Contact process") and hydrating the sulphur trioxide so produced in the presence of strong sulphuric acid.

Hitherto the recovery of the sulphur from blende roasting has not received in this country the attention its great importance demands, and in this respect the British smelters are behind those on the Continent and in America, who have for some years given considerable attention to the production of sulphuric acid as a valuable secondary product of zinc smelting. As recently

<sup>1</sup> H. M. Ridge, "The Utilisation of the Sulphur Contents of Zinc Ore," Journal of the Society of Chemical Industry, 1917, vol. xxxvi, pp. 676-684. pointed out by Moulden, it is now the practice in most European and many American works to carry on the blende roasting in conjunction with the manufacture of sulphuric acid, and this for two main reasons: (I) the restriction imposed by legislation in most thickly populated districts upon the discharge of sulphurous gases into the atmosphere, and (2) the value of sulphuric acid in such localities, due to the fact that they are consumers of the acid, and it therefore pays to utilise the sulphur.

It is not uncommon in Europe to find the roasting and the manufacture of sulphuric acid carried on in one district where the call for the acid is considerable, and the roasted ore distilled in another where conditions as to fuel, clay and labour are the more favourable. Economic considerations govern, of course, each individual case, and this system has reached its greatest development in Belgium and Germany, largely owing to the abundant and cheap facilities for transport afforded by the various canal systems.

Year.	Raw blende roasted.	Sulphuric acid reduced to 50° Bé.	Sale	value.
	Metric tons.	Metric tons.	Total marks.	Metric ton of 50° Bé. acid.
1887 1891 1895 1899 1903 1907 1911 1912	53,882 66,236 84,857 123,602 187,596 421,006 411,352	21,013 32,676 33,229 64,029 104,268 139,840 213,317 254,008	479,000 746,000 778,000 1,074,000 1,728,000 2,187,000 3,025,000	Marks. 22-81 22-85 23-43 16-77 16-62 15-65 14-18

SULPHURIC ACII	<b>PRODUCTION</b>	IN	Upper	STLESIA.
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To illustrate the importance of the utilisation of the sulphur of zinc ores, Ridge gives the above figures for the output for Upper Silesia prior to the war. In normal times this district produces about 60 per cent. of the spelter made in Germany, but a considerable amount of calamine ore is still available there, so that the maximum production of sulphuric acid from blende has not yet been reached; the tonnage of calamine treated is, however, steadily decreasing, but this is compensated for by an increase in the amount of blende treated, and permits of an increasing spelter and acid production. The last figures available are for 1912, and the table on page 113 shows the results for every fourth year since 1887.

The rapid annual increase in the production of sulphuric acid in the Upper Silesia district in recent years is shown by the following statement. In 1900 the production of sulphuric acid per ton of crude zinc produced amounted to only 0.08 metric ton; in 1905 it had increased tenfold to 0.85 metric ton, and in 1913 it still further increased to 1.34 metric tons.

"Prior to the war six works in Silesia still used their old reverberatory furnaces, so that not all the sulphur could be utilised, but for some years factory legislation has prohibited the emission of noxious fumes, and as the plants become worn out they have to be replaced by modern installations. The fumes from the reverberatory furnaces are scrubbed with milk of lime which is sent to waste. Five plants have lead chambers and make acid of  $50-55^{\circ}$  Bé.; this is generally concentrated in cascades or Kessler apparatus and in recent years largely in Gaillard towers. Three works have contact plants as well as lead chambers. There was in 1912 a total of 48 lead chambers. "Of the total production of acid.

41,055 metric tons was sold as acid of 50° Bé. 114,346 metric tons was sold as acid of 50°-60° Bé. 42,349 metric tons was sold as acid with 98-100 per cent. H<sub>2</sub>SO<sub>4</sub>. 216 metric tons was sold as oleum with 20 per cent. SO<sub>3</sub>, 4,774 metric tons was sold as SO<sub>3</sub>. and in addition 2,855 metric tons of liquid SO<sub>2</sub> was made.

"The acid is used for making superphosphates, sulphate of ammonia, dynamite, and guncotton, and for refining mineral oil. It is distributed by rail over a wide area, some going into Russian Poland, Austria-Hungary, and even to Roumania.

"The position in the zinc smelting districts in Western Germany is analogous, but the make of acid there is larger in proportion to the production of spelter, because there is no local supply of calamine. The newer smelting works have been placed on navigable waterways so that freights on raw materials and finished products are low. The chamber process is used in all the works except one, which has a contact plant ; there is also one installation making liquid sulphur dioxide.

"In 1913 in Germany 554,760 metric tons of blende was roasted for making sulphuric acid; of this 87,439 tons was imported from Australia and 56,181 tons from other countries.

"In Belgium blende is mainly roasted by the chemical manufacturers, who retain the sulphur and receive from the zinc smelter in addition a payment of 6 to 8 francs per 1,000 kilos. for roasting the ore. This was facilitated by the low freights on the canals, which reduced transit charges to a very low figure. In Belgium 65 per cent. of the total production of sulphuric acid is made from blende; the amount of zinc acid is nearly 400,000 tons."<sup>1</sup>

In America, fourteen zinc smelters make sulphuric acid, mainly by the contact process. With the movement of the zinc smelting industry to the eastward, which has taken place in recent years in America, the separation of blende roasting and zinc distillation has become more pronounced, as it has been for a long time in Europe.

It is now regarded as good practice to roast the blende at some convenient centre for the distribution of the sulphuric acid, and then to reship the roasted ore to a suitable place for zinc distillation. This is now being done by many of the larger concerns.

The American production of sulphuric acid from blende, calculated as  $60^{\circ}$  Bé. acid, in modern times is as follows <sup>2</sup>:

Year.					Production in short tons (2,000 lb.).	3
1911	.,	••			230,643	
1912					292,917	
1913					296,218	
1914				• •	411,911	
1915		••	• •	••	484,942	

The average price realised in 1915 was 8.85 dollars per short ton. The use of the contact process for the treatment of the sulphur fumes from blende has made its biggest strides in the United States because the smelters are largely able to rely for their ore supplies upon the produce of one or more home mines, and are not dependent upon small lots of ore shipped from various parts of the world, as has been the case in this country and on the Continent. Consequently, the American smelters have been

<sup>1</sup> Ridge.

<sup>2</sup> ibid., loc. cit. p. 683.

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able to make provision for eliminating any harmful ingredients which may be present in the ore which they expected to be treating over a long period. The American smelters also have the advantage of having practically no hand-rabbled furnaces, all the blende roasting being done in the Hegeler furnace. In the United Kingdom, sulphuric acid has hitherto only

been made from zinc ore roasting in three plants, and it is estimated by Ridge that their combined output of acid does not exceed 25,000 tons of 140° Tw. acid a year. This amount corresponds with a production of about 10,000 tons of virgin spelter, which is approximately one-third the production of spelter in this country in 1913. Part of this metal was made from calamine, but since the available supplies of this ore are steadily decreasing, it is only a question of a comparatively short time before the whole of the virgin spelter will have to be smelted from zinc blende. This country has suffered badly in the past from the existence of wasteful and harmful metallurgical processes in certain areas, and especially in the treatment of zinc ores it has been customary to roast the sulphide ore in reverberatory furnaces from which the sulphur fumes cannot be used, so that the sulphur is wasted and the atmosphere polluted. While it is true that there has been some increase in recent years in the utilisation of the gases from blende roasting for the manufacture of sulphuric acid, it is much to be regretted that the Inspector of Alkali Works has had to report that considerable extensions of roasting plants for zinc ores were erected during 1915, and that arrangements had actually been made for further extensions in 1916, in which no provision whatever had been made for the recovery of the sulphur.

It is very desirable that such a procedure should be prohibited by legislation. That the matter is, however, receiving some attention is evident from the Inspector's latest report, in which it is stated that further progress has been made in the utilisation of the sulphur fumes from blende roasting for producing sulphuric acid, in spite of difficulties connected with the working of mechanical roasting furnaces and the scarcity of suitable labour for working the necessary hand furnaces. In the newest installations, the mechanical reverberatory Ridge furnaces have been adopted with satisfactory results.

It is necessary to remember that in 1913 the total consumption

of zinc in this country amounted to no fewer than 224,000 tons, of which 74 per cent. was imported.

After allowing for the metal produced by the British smelters, the imported metal was about 166,000 tons of spelter in addition to zinc in other forms. If, as pointed out by Ridge, this quantity were all made from blende, the roasting fumes could be used to produce annually 400,000 tons of 140° Tw. acid. There is no reason why this should not be done and the corresponding quantity of brimstone and non-cupreous pyrites, and pyrites with small copper content, now used for sulphuric acid production, displaced. Before the war the cost of making 140° Tw. acid from zinc ore roast gases in this country was only between 8s. and 9s. per ton, so that the operation is remunerative. Zinc ore must be heated because spelter is required, and if the roasting is not done here it will be done elsewhere. Cheap sulphuric acid has always been an important factor in the chemical industries, and the resources of the Empire should be used for its production within the Empire.

Although the main commercial use for the sulphur fumes from blende roasting is the manufacture of sulphuric acid, they are also utilised to a limited extent for making sulphites and liquid sulphur dioxide.

"Aluminium sulphate has been made at Flone in Belgium by passing the roaster gases into large chambers excavated in the hill-side and filled with alum shale.<sup>1</sup> At Ampsin this method was also used for making alum with gas from reverberatory furnaces; it seems that sulphite is first formed, and this readily oxidises to sulphate.

"The manufacture of liquid sulphur dioxide was started by Grillo at Hamborn in Westphalia, because the fumes from the roasting furnaces were low in sulphur dioxide, and it was, at that time, considered impossible to utilise them for making sulphuric acid. The furnace gases pass to a scrubbing tower sprayed with water, which dissolves the sulphur dioxide, and the liquor gravitates to a series of pans, which are placed over the burners, the heat of which is sufficient to drive off the sulphur dioxide gas, which, after being cooled, is compressed and liquefied at a pressure of 7 atmos. In Germany two plants are in operation, viz., one at Hamborn and another at Lipine in Silesia, but, in this country, the method has not been employed on the

<sup>1</sup> Ridge, loc. cit. p. 682.

fumes from zinc ore. The demand for liquid  $SO_2$  is limited."

Lead and Silver.—These metals form important by-products in the smelting of zinc-lead ores, such as the Broken Hill concentrates, to which reference has already been made (p. 53).

When the ores contain much lead and silver, practically the whole of the silver and most of the lead will be found in the residues, which in this case are of commercial value.

They are usually concentrated, after grinding, by simple water-concentration in jigs and on tables, and the enriched material sold to lead smelters. The presence of lead is necessary in residues containing silver, as it acts as a collecting agent for the silver, consequently the lead content, as well as the silver, is taken into account when determining the price to be paid for the zinc blende. A deficiency of lead reduces the value of the ore because it causes loss of silver.

Zinc Fume.—This is another important by-product in zinc smelting, and consists of a mixture of finely divided zinc and zinc oxide. In America, zinc fume is called "blue powder." This product has increasing commercial value and its utilisation is dealt with later (p. 171).

Cadmium.—This metal is also obtained as a by-product. Cadmium occurs in small quantities, usually less than 0.5 per cent., in many zinc ores, such as the sulphide and carbonate. and practically all the cadmium of commerce is obtained from such ores. The metal is reduced by carbon and carbon monoxide at a lower temperature than zinc; consequently, in the process of extracting zinc from its ores, the cadmium, is obtained in the first portions of the product of the distillation, partly as metal and partly as oxide. It collects in the condensers and prolongs during the first two hours, and the product may contain from 5 to 8 per cent. of cadmium. This is submitted to redistillation to obtain the metal of commerce. Upper Silesia is the chief centre of cadmium production; some is produced in Great Britain, and a small quantity in the United States. The amount capable of being produced in Upper Silesia is comparatively large, but there has never been an important demand for the metal, and consequently its recovery has been undertaken by only a few concerns, and in limited quantity, most of the product from which it might be obtained being permitted to remain in the spelter. The consumption of the metal is small. Its chief use is in the preparation of certain "fusible" alloys, in which advantage is taken of its low melting point. It is also used to a limited extent in electroplating. The metal possesses some very useful properties, and its electrodeposition may in the future find a more extended application. Compounds of cadmium are used in photography and also as pigments.

Owing to the limited demand, the metal is comparatively high in price, but as it occurs fairly abundantly in nature, this would doubtless be reduced if the demand increased.

Residues from Retorts.—The exhausted residues drawn from the retorts are, in the case of clean ores, usually sufficiently free from zinc to be thrown away. The composition of these residues naturally depends, of course, on the composition of the ores, and with average ores they may be said to contain as a rule from 4 to 8 per cent. of zinc. They contain carbonaceous matter in sufficient quantity to permit of profitable utilisation, and attention has already been drawn to the attempts that have been made in America to turn them to account.

When the ores contain much lead and silver, practically the whole of the silver and most of the lead will be found in the residues, which in this case are of commercial value.

They are usually concentrated after grinding by simple waterconcentration in jigs and on tables, and the enriched material is sold to lead smelters, who also value them for the iron they contain, which acts as a flux in smelting.

The carbon content in the lead residues or slack is also a cheap reduction material.

# The Cost of Zinc Production

The combined cost of roasting and distilling zinc ore necessarily varies in different smelting centres, as such conditions as character of ore, cost of raw materials, labour, fuel, distance from market, etc., differ with locality. The output, or works capacity, also has an important bearing on the cost of the metal produced. Practically two and a half tons of ore give one ton of spelter.

Pre-war British practice was to roast blende in reverberatory hand-rabbled furnaces at a cost of 11s. to 12s. 6d. per ton of ore.

This figure compares very favourably with Continental practice

in modern mechanical furnaces, as shown by the working costs given below.

In the larger installations in the Swansea district the pre-war smelting charge of  $f_{2}$  15s. od. to  $f_{3}$  os. od. may be taken as the inclusive cost, and as covering the roasting of the ore.

The following approximate figures have been given by J. Gilbert,<sup>1</sup> as the average cost of smelting one ton of ore at modern works on the Continent.

The cost of roasting one ton of blende is :

						un b	r ton of roasted lende. s. d.
Superinten		••					9
Rolling, &c		••					3
Roasting f	urnace	work		••			4 10
Coal	••	••				:	2 9
Repairs	••	••	••				2
Sundries	••	••	• •	• •	• •	••	9
Various con		ions					7
Crushing, &	kc.	••	••	••	••		Ġ
						-	
		Te	otal co	st	••	10	7

Details.—From 2,300 to 2,500 tons of crude blende produced 2,000 to 2,200 tons of roasted ore. Fuel consumption was 23 to 25 per cent. of furnace coal per ton of roasted blende. The cost of one ton of coal was 12s. on the basis price given below. Loss of metal in roasting, 0.95 to 1.0 per cent. Maximum value of sulphuric acid realised 9s. Actual cost of roasting, per ton, 1s. 7d.

The above figures refer to Rhenish roasting furnaces producing about 8 to 8.5 tons of roasted blende when working normally. With crude ore containing from 23 to 25 per cent. of sulphur and about 0.5 per cent. of lime, and retaining after roasting about 1.1 per cent. of sulphur, the yield of sulphuric acid from the extractable sulphur is from 85 to 92 per cent., normally about 90 per cent.

Cost of distillation of zinc ore at a modern Rhenish works with a producing capacity of 10,000 to 12,000 tons per annum:

<sup>1</sup> "Costs and Profits of an up-to-date Spelter Works," J. Gilbert, *The Mining Journal*, London, 1916, vol. cxiv, pp. 480-481, 496-498. (Very complete details of costs are given in this article.)

#### ZINC SMELTING

		Per ton ore treat			
			<i>s</i> .	đ.	
Management, office, &c			9	6	
Generators (wages, coal), reductive coal			17		
Repairs of furnace				3	
Fireproof material, tempering	• •	••	5	0	
Zinc stores and sieving of zinc dust				6	
Various contributions to funds, &c.	• •	••	Ι	0	
Sundries (water, light, &c.)			2	9	
Ore mixing				9	
General expenses			3	6	
			_		
Each ton of ore treated : total actual	$\mathbf{costs}$		40	9	

Details.—Ore treated, 2,000 to 3,000 tons per month. Production, 1,000 to 1,400 tons of spelter and 100 to 140 tons of zinc dust monthly. Percentage of zinc contained in the roasted ore, 50 to 51 per cent. Loss in smelting (ore poor in lead), 12 per cent. Durability of retorts, forty to forty-five days. Coal, furnace, and tempering, 115 to 120 per cent. on ore weight, at 105. 6d. to 105. 9d. per ton delivered at works. Basis price main coal, 135. 9d. delivered at works. Reduction coal, 40 to 45 per cent. of weight of ore.

The ordinary life of a zinc furnace is about six years, but some regenerative furnaces have given good results, even after eight or ten years.

The costs of repairs vary from £150 to £300,

Considerable discussion has taken place since the outbreak of war as to the possibility of smelting a large proportion of the Broken Hill zinc concentrates in the United Kingdom.

Without entering into the many problems involved, the following estimate for the treatment of the concentrates in Swansea recently put forward may prove to be of interest; an allowance, equivalent to one-half of the cost of roasting, is made in this estimate for the recovery of the sulphur as sulphuric acid.<sup>1</sup>

The estimate is based on a recovery of 85 per cent. of the zinc, 60 per cent. of the lead, and 50 per cent. of the silver from concentrates containing zinc 47 per cent., lead 8 per cent., and silver 10.5 oz. per ton. On this basis, the spelter recovered would be 0.4 ton for each ton of concentrate treated.

<sup>1</sup> Quoted in the Bulletin of the Imperial Institute, 1916, vol. xiv, p. 68, but original source not given.

			Cost	t per i	on of	ore,
				£ s.	d.	
Roasting	••	••		ື_3	9 <del>1</del>	
Furnace labour	••	••		12	2	
Fuel and reducing coal		••		I O	5	
Retorts and condensers		• •		4	5 81	
Repairs				Í	2	
Administration and overl	nead cha	rges	••	2	0 <del>]</del>	
				2 1	31/2	
Cost of concentrates at w	orks	••	••	4 I 5		
Total				7 0	тţ	
Deduct value of residue les	streatm	entcos	sts	. 12	8	
Net t	otal	••	••	£6 7	5뉢	

## The Conditions of Labour in Zinc Smelting

The work connected with the distillation of zinc is very arduous, and considerable skill is required in conducting the process, especially in charging the retorts, an operation which needs great dexterity.

In the chief zinc-smelting centres the workmen are specially trained, and in many cases the knowledge required for the more important parts of the process has been handed on from father to son through several generations of workers. On the Continent, special provision has been made to train the men required so that the output shall not suffer from lack of skilled workers.

There is a general agreement that the labour conditions in this country, as compared with the Continent, are detrimental to output. It is not, however, suggested that this is due to inferiority of the men individually.

Unquestionably the most difficult part of the problem connected with the development of the British industry is the training and organisation of the labour required for the smelting process. Difficult though these are, they should be undertaken without delay, for America has shown that they can be done, and done rapidly when necessary.

The system of payment of wages adopted in this country differs from that in use on the Continent. In the British spelter works the Datal system is in use, a fixed rate of wage being given per shift, according to the duties to be performed. On the Continent the system of giving premiums has been attended with marked success.

At the great Belgian zinc works of La Vieille Montagne, the smelters and mill men receive, in addition to a fixed wage, a premium calculated on the output, and a special premium is also given for unusual energy. In some cases the firemen receive a similar premium, based on the time their furnace lasts without repair. In other cases, the workmen receive a premium when they obtain from the ores a greater amount of metal than that which they are calculated to yield. Two-thirds of this premium is paid periodically with the regular wage. The remaining third is retained until the end of the year, and it is not paid then unless the workmen have worked regularly throughout the year.

In some of the German works additional premiums are paid on the production of zinc dust, of metallic lead recovered from the distilling furnace, and the life of the retorts.

The tendency of zinc smelters within recent years has been to substitute, as far as possible, mechanical labour for manual labour. Especially is this the case in regard to roasting furnaces, but in the case of the distillation process, although mechanical charging and discharging appliances have been introduced, they have only been adopted to a very limited extent. The various operations connected with the distillation process do not lend themselves readily to mechanical devices. However, attention is being given to the possible application of mechanical appliances to the manipulation of zinc distillation furnaces, and a certain amount of success has been attained, more particularly on the Continent and in America.

As previously stated, machine-made retorts have now very largely replaced those made by hand, thus effecting a considerable saving in manual labour.

## CHAPTER VII

#### OTHER METHODS OF ZINC PRODUCTION

## The Electric Smelting of Zinc Ores

WHILST practically the whole of the zinc of commerce is produced by distillation, great efforts have been made in recent years, and large sums of money spent, in the endeavour to simplify, expedite, and cheapen extraction, and in particular to render the process of zinc production continuous.

It is recognised that the distillation process leaves much to be desired, because the heat is applied uneconomically, as it has to pass through the walls of the retorts, and in consequence these retorts must be relatively small, restricting the output of metal, and much hand labour is required in treating the ore.

Of all the various newer processes that have been devised and experimented with for the extraction of zinc from its ores only two may be said to have approached commercial success, viz.; (I) electro-thermal methods, or electric smelting, and (2) hydrometallurgical methods. In the electro-thermal methods the distillation is continuous, the reduction and distillation being effected by heat produced within the reducing vessel or furnace itself; and in hydro-metallurgical, or wet methods, the zinc is first dissolved and then recovered from solution by electrolysis.

Both these methods have been applied to the recovery of the metal in low grade ores and in ores which cannot be satisfactorily treated by the usual distillation method. The electro-thermic production of zinc in the electric furnace was first attempted, in 1883, by the Brothers Cowles, who developed the resistance type of furnace originated by Despretz in 1849, in which a core of carbonaceous material in the charge itself carries the current in a horizontal direction. In 1901 C. P. G. De Laval erected the first electric furnace for smelting zinc on a commercial scale, and four years later works were erected in Sweden to carry out his process. Since that time a considerable amount of attention has been given to electric furnaces for smelting zinc ores.

As pointed out by Professor Gowland,<sup>1</sup> " the chief drawbacks that impede the commercial success of the application of the electric furnace to the smelting of zinc ores are the cost of the current and of the electrodes, the loss of metal and the difficulty of obtaining a fair proportion of the zinc as metal and not as oxide, which has to be re-treated."

In spite of these drawbacks, the electric smelting of zinc ores has held the attention of metallurgists for a long time, and during recent years a large amount of work has been done on the problem of treating, not merely the high grade ores that are easily distilled in the ordinary retort furnaces, but also the low grade and complex ores that can hardly be treated at all by existing methods.

In discussing the electric smelting of zinc ores, Prof. A. Stansfield <sup>2</sup> considers that the first point to make clear is the great difference between the old practice and the methods attempted by the electro-metallurgist. In the usual retort, the charge of roasted ore and coal is heated gradually for a number of hours, driving off first the moisture and the hydrocarbons from the coal, then the carbon dioxide resulting from the reduction of easily reducible metals such as iron and lead, and finally, when a temperature of more than 1000° C. has been reached, the zinc vapour itself with its equivalent of carbon monoxide.

Under these conditions the condensation of the zinc vapour is satisfactory, and a large proportion of the metal is obtained in the molten condition. This operation could no doubt be reproduced in an electric furnace, and would have the advantage that somewhat larger retorts could be employed ; but the electric furnace inventor is not content with so moderate an attainment : he wishes to change the whole process from the present step by step method to a continuous smelting operation in which the ore and reducing carbon shall be fed into the furnace at one point, the zinc flow out of the condenser, in the molten state, at another point, the slag be tapped off from a third point, and lead bullion.

<sup>1</sup> "Metallurgy of Non-Ferrous Metals," 1st. Edit., London, 1914, p. 396.
<sup>2</sup> A. Stansfield, "Electric Furnaces as Applied to Non-Ferrous Metallurgy," Journal of the Institute of Metals, 1916, vol. xv, p. 289.

carrying any gold and silver values, shall flow out at a fourth opening in the furnace.

The task thus set is by no means easy; if the ore mixture goes without preparation into the smelting chamber, the moisture, hydrocarbons and carbon dioxide will come off in admixture with the zinc vapour and carbon monoxide, and the zinc will condense from this mixture mostly in the form of a blue powder. By a preliminary heating of the ore mixture in a separate chamber the moisture, hydrocarbons and carbon dioxide can be removed to a large extent, but it is difficult to effect their complete removal. Thus it appears that there are considerable difficulties to be

Thus it appears that there are considerable difficulties to be overcome before a successful electric furnace process can be developed.

One difficulty, inseparable from the ordinary process of zinc smelting, is the need for an almost perfect roast of the sulphide ore, as a preparation for the distillation process.

Stansfield considers that the electric furnace process, on the other hand, holds out the hope that this roasting operation can be dispensed with, or at least that it need not be nearly so thorough. This possibility depends on the removal of the sulphur in the electric furnace in combination with metallic iron, or more cheaply with calcium supplied in the form of lime.

This latter reaction has been studied by O. W. Brown and W. F. Oesterle,<sup>1</sup> who find that it takes place very completely, in the electric furnace, according to the equation

$$ZnS + CaO + C = Zn + CaS + CO.$$

Early experimental work by W. R. Ingalls at the McGill University confirmed the opinion that, if electric smelting is to offer any advantages over distillation in retorts, the process must be continuous, and all modern furnaces are constructed on this principle. In many of the electric furnaces now in use the energy is applied with great ingenuity and high efficiency is obtained, whilst efforts are made to reduce the electrode consumption to a minimum.

The reduction in the electric furnace seems to take place more rapidly than in retort smelting, but the reaction between the carbon and carbon dioxide does not appear to occur to such an extent in the former as in the retort. Hence the electric furnace

<sup>1</sup> "The Electric Smelting of Zinc," Transactions of the American Electrochemical Society, 1905, vol. viii, p. 171.

contains an atmosphere comparatively rich in carbon dioxide, so that a larger amount of fume (blue powder) is formed than when the retort furnace is employed.

Cote and Pierron, Johnson and others have attempted, with some success, to solve the carbon dioxide problem by such means as passing the gases through columns of incandescent carbon. But while progress has been made, the discovery of how to avoid oxidation of the zinc deposits, as formed under the conditions prevailing in electric smelting, is still the problem which metallurgists have to solve in connection with this method of zinc smelting.

The continuity of operation in the electric furnace implies discharging the residue as a slag that will flow, and there has been a tendency for inventors of electric zinc furnaces to render the charge fusible, so that fluid slags may be tapped as from cupolas. This condition, however, prohibits any great excess of carbonaceous material in the charge, and accounts for the higher percentage of carbon dioxide frequently found in continuously operated furnaces.

Among the various types of electric furnace now in use, those of De Laval, Cote and Pierron, and Johnson may be mentioned. The first two may be selected as typical, and as involving the two types of electric furnace; De Laval employs the electric arc, and Cote and Pierron slag resistance, as means for converting electric energy into heat.

The De Laval process, which has been carried out commercially for some years at Trollhättan and Sarpsborg, in Sweden, develops heat by means of the arc, current being generated from water ' power at prices variously given as from 38s. to 50s. per electrical h.p.-year.<sup>1</sup> The works are equipped for 18,000 electrical horsepower and produce over 6,000 tons of refined zinc annually.

The process is conducted in two operations, the first being the smelting of the roasted ore in an arc furnace for the production of a coarse metal containing zinc, lead and other metals, and the second the refining of this coarse metal by distillation in another arc furnace.

Much of the zinc is obtained as fume or dust.

The furnaces are of the resistance type, with one large vertical carbon electrode passing through the roof, the other electrode being a carbon block in the bottom of the furnace. Each furnace

<sup>1</sup> Sulman, loc. cit.

has a capacity of about 3 metric tons and smelts nearly 3 tons of ore in twenty-four hours.

The complex argentiferous zinc-lead sulphide ore is first roasted to expel most of the sulphur. The roasted ore containing about 7 per cent. to 8 per cent. sulphur is then mixed with anthracite or coke and flux and charged through a hopper into a closed electric "melting" furnace, where most of the zinc and some of the lead are volatilised, and condense chiefly as crude spelter high in lead, and partly as blue powder, which has to be re-treated.

The other part of the lead is reduced to metal and is tapped out with the slag. It contains a considerable proportion of the silver present in the ore. Some matte (fused sulphides) is formed, and this and the slag contain some of the lead, zinc and silver. The crude spelter containing lead passes to the electric refining furnace, where the zinc is distilled, producing, on condensation, spelter of high grade, and a further quantity of zinc dust, leaving the remainder of the lead and silver as base bullion. Two melting furnaces supply one refining furnace.

The company owning these Swedish works reported recently that its smelting operations have not yet proved commercially profitable; considerable progress has, however, been made and it is hoped that things will eventually turn out well. About half the cost of smelting is for electric current, and it is thus evident that very cheap electric power is essential for the commercial success of the process.

It would appear that the solution of the difficulties connected with the condensation of the zinc are to be sought, not in the condenser proper, but in the character of the gas delivered to it. The attempt to condense a commercial proportion of the vapour resulting from the reduction of zinc oxide has so far failed, this being the crucial point of electric zinc ore smelting.

On the basis of ore alone the consumption of power at Trollhättan, according to report, was 2,078 kilowatt-hours per 100 kilogrammes of ore, but for every ton of ore smelted about two tons of zinc powder had to be resmelted.

The smelting of 1,000 kilogrammes of ordinary zinc ore (25-30 per cent. zinc) is reckoned to require from 900 to 1,000 kilowatt-hours. Each furnace smelts about 2,800 kilogrammes of ore in twenty-four hours.

The Cote and Pierron process is carried out on a small scale in France, notably at the Arundy Works in the Pyrenees, which have been in operation since 1904; experimental work with this process has also been carried on since 1914 at Ugine and Iperre, in Savoy, and at Quenean in Belgium.

An important feature of the process is the smelting of blende in the raw state, that is, without previous roasting to remove sulphur. Whilst simplifying the metallurgy of the process, this method increases the difficulties of operation of the electric furnace. The Cote and Pierron process is based on the fact that iron replaces lead in lead sulphide at a comparatively low temperature, and zinc in zinc sulphide when the temperature is increased. It is claimed that the process effects a complete separation of the zinc and lead. The furnace is a combined arc and resistance furnace. It is circular, with sides and bottom lined with graphite, thus giving a conducting lining; the roof is a low dome of fire brick. A carbon electrode, which can be raised or lowered passes through an opening in the centre of the roof; the other electrode, a cone of graphite, projects from the hearth. The furnace is charged through the roof, and the lead, slag, and iron sulphides are tapped through an aperture in the side. The volatilised zinc passes through an outlet in the upper part of the furnace to the condenser, which consists of a cylindrical, shaft-like chamber of fire brick filled with coke or anthracite, and provided with a taphole at its base for the discharge of the condensed zinc.

The charge, consisting of a mixture of 200 kilogrammes of ore with iron turnings, and lime as flux, is introduced into the hot furnace, and the first reaction of iron on lead sulphide is effected at a relatively low temperature. The resulting lead is then tapped. The temperature is now raised and the decomposition of the zinc sulphide by the iron brought about. The zinc distils over, and is condensed in the condenser, the carbon in the upper part of which is kept at a red heat, to prevent as far as possible the formation of zinc fume. Finally, the iron sulphide and the slag are run out. At the Arundy Works a furnace of 350 kilowatts, with alternatingcurrent at 55 volts, treats one ton of blende (35 per cent. zinc) per 95 to 100 horse-power-days.

It is claimed that not more than 2 per cent. of zinc remains in the slags.

In America a considerable amount of experimental work has been done with W. McA. Johnson's electric furnace at Hartford, Connecticut, and it is stated that arrangements have been made to erect a roo-ton commercial plant at Keokuk, Iowa, for the treatment of very complex ores. This is a continuous process with furnace of the resistance type, in which the charge carries the current.

The charge is heated to about 900° C. in a continuous preheater before reaching the furnace.<sup>1</sup> To prevent the formation of blue powder, the carbon dioxide formed in the smelting zone is rendered innocuous by passing the gases from the furnace through an electrically-heated carbon filter, whereby the carbon dioxide is converted into harmless monoxide.

This process has been investigated by the Dominion Government with a view to its application in British Columbia, but apparently complete success has not yet been reached.

Another process that is claiming attention is the Snyder process, which has been applied to the treatment of argentiferous zinclead ores. The ore is roasted to oxide, and fluxes added so that the mixture will melt at about 1000° C. The molten mixture is then treated in an electric furnace and results in the reduction of the metals present. The lead, alloyed with the silver, collects below the slag, and is tapped off, and the zinc which is oxidised and volatilised is condensed in brick chambers.

Although electric zinc smelting has now passed beyond the experimental stage and become a commercial process, it is being continually investigated by those especially interested in this method of smelting zinc ores. An expert on zinc production, J. C. Moulden,<sup>2</sup> has recently expressed the opinion that, given favourable primary conditions and the inevitable improvement to be brought about by experience, the electrothermic method of distillation will in the future substantially influence the production of zinc.

# Hydro-metallurgical Processes of Zinc Production

Since Parnell took up the question of treating complex zinclead ores at Swansea in 1881, many wet methods of zinc extraction have been suggested and experimented upon, but until quite recently none have met with commercial success owing to their inability to produce metallic zinc.

<sup>1</sup> Journal of the Royal Society of Arts, 1916, vol. lxiv, p. 513.

<sup>2</sup> Ibid.

Unlike most metals, zinc cannot be precipitated from its solutions by common metals, and if other precipitants are used and it is obtained as oxide, this must be mixed with carbon and treated by a distillation process in order to obtain the zinc as metal. Thus Parnell's process consisted in roasting the ore to sulphate, leaching with water, evaporating the purified zinc sulphate solution to a paste and adding powdered zinc blende. This mixture was then heated to produce zinc oxide, which was reduced in retorts and distilled. The argentiferous lead residue left in the vats was sold to lead smelters for the extraction of the lead and silver.

The difficulty of obtaining the zinc in the metallic state has been the main reason for the slow development of wet methods of zinc production. However, where formerly it did not pay to leach out zinc in the form of sulphate, owing to the limited market for the salt and the prohibitive cost of converting it into oxide, the growing demand for white pigments free from lead has made it possible to avoid the necessity of extracting the zinc as metal by crystallising the dissolved zinc as sulphate.

Thus, as the result of the increasing demand for zinc sulphate for the production of "lithopone," to which reference is made on p. 193, the unit of zinc in crystalline sulphate has a considerably higher market value at present than a unit of zinc in the form of oxide for smelting purposes.

More recently, hydro-metallurgical processes have been devised in which the zinc after having been obtained in solution, either as sulphate or chloride, is precipitated in the metallic state by electrolysis; but while the difficulties which formerly attended the precipitation of electrolytic zinc have so far been overcome as to form the basis of recent methods, the high cost of electric power has operated against the commercial success of most of these processes.

Létrange was one of the earliest workers in the production of zinc by electro-deposition; in his process the crushed blende was carefully roasted at a low temperature to produce zinc sulphate, which was dissolved with dilute sulphuric acid. The solution was then electrolysed, using an anode of lead (or carbon) and a cathode of zinc.

Electrolytes of zinc chloride solution are said to be more economical in electric current than solutions of zinc sulphate, the electromotive force necessary for the decomposition of the former being less than for the latter. In practice, however, it has been found to be more satisfactory to extract the zinc as sulphate than as chloride, and in most of the wet processes now in use the electrolyte consists of zinc sulphate.

Considerable attention has been given during the past few years to the electrolytic separation of zinc from its ores, especially so-called complex ores, and a specially pure zinc is now being satisfactorily produced by this process.

Compared, however, with smelting, the amount of zinc produced by electrolytic separation is very small, though the importance of the latter process is gradually increasing in districts where the special nature of the ore renders the application of hydro-metallurgical processes on a commercial scale possible. There is, however, little prospect that wet methods of zinc production will be sufficiently successful on a commercial scale to enable them to compete with the distillation processes.

The only commercial processes in the electro-metallurgy of zinc by direct wet methods appear to be those of Nahnsen, of Hoepfner, and of Dieffenbach.<sup>1</sup>

The Nahnsen process has been employed at Lipine, Silesia, since 1893, the electrolyte used being a solution of the double sulphate of zinc and magnesium. The Hoepfner process is in operation at Duisburg, in Germany, and two plants were erected in 1914 at Kristiania and Balestrand, in Norway, for the treatment of Broken Hill flotation concentrates.

A modification of the method originally devised by Hoepfner has been employed with considerable success in the United Kingdom at the works of Messrs. Brunner, Mond and Co., near Northwich, Cheshire, where considerable quantities of zinc of high grade are now made and employed for the manufacture of brass for cartridge cases and other articles requiring a highly ductile alloy.

The ore is roasted to convert the zinc into oxide, which is then transformed into zinc chloride by carbon dioxide and a solution of calcium chloride, waste calcium chloride liquors from the Solway ammonia-soda process being used for the purpose. This results in the solution of the zinc as chloride and the precipitation of calcium carbonate. The zinc solution is purified by a series of operations analogous to those devised by Hoepfner.

<sup>1</sup> Abstract of paper by R. Sylvany, Journal of the Institute of Metals. 1914, vol. xii, p. 318. The iron and any manganese are precipitated by means of chloride of lime and calcium carbonate, and the other metals, copper, lead, etc., by the addition of zinc fume to the clear solution. The purified solution is electrolysed, using revolving iron disks as cathodes and carbon anodes enclosed in cloth diaphragms, a current density of 30 amperes per square foot of cathode surface being employed. The solution for electrolysis should contain from 0.08 to 0.12 per cent. of free hydrochloric acid.

The products of electrolysis are metallic zinc and chlorine, the latter being subsequently converted into bleaching powder. The recovery of such a valuable by-product as chlorine from a waste material is a very important factor in the economic success of this process at Messrs. Brunner Mond's works. The zinc produced has a purity of about 99.96 per cent.

The Dieffenbach process is applied to a Westphalian iron pyrites, containing 8 per cent. of zinc, which is converted into chloride by roasting with sodium chloride, and extracted by leaching with water. The residue, which is said to contain only 0.5 per cent. of zinc, is smelted for iron, whilst the aqueous solution of zinc chloride is electrolysed in double-compartment vats, the anode compartments being completely closed. The liberated chlorine is employed in the manufacture of calcium hypochlorite.

Since the outbreak of war there has been a very important development in the electrolytic production of zinc in America, especially at Anaconda and Trail. The processes being used in American plants are based on sulphuric acid leaching, and subsequent electrolysis of the zinc solution, using lead anodes. The largest American plant for electrolytic zinc production is that of the Anaconda Company, at Great Falls, Butte, which when complete will produce 35,000 tons of electrolytic zinc annually.<sup>1</sup> The ore is concentrated, chiefly by flotation, and is then roasted until the sulphur content is 2 or 3 per cent., mostly as sulphate.

The temperature must not exceed 732° C., in order to avoid the formation of zinc ferrite. The roasted residue is leached with spent electrolyte to which a sufficient quantity of sulphuric acid has been added. A little manganese dioxide, followed by

<sup>1</sup> W. R. Ingalls, Transactions of the American Electrochemical Society, 1916, vol. xxix, p. 347. powdered limestone, is added to remove iron, arsenic and antimony. Lead, silver and gold remain in the residue, and the only impurities in the filtrate are copper and cadmium, which are precipitated by metallic zinc. Formerly zinc fume was used to precipitate the cadmium, but difficulties were encountered, and the plan now adopted consists in running the clear solution through tube mills containing zinc balls.

After filter-pressing, the solution is electrolysed with lead anodes and aluminium cathodes. The current density is 20 to 30 amperes per square foot of cathode surface (220 to 330 per sq. m.), and the current efficiency 93 to 94 per cent. The cathodes, which are stripped every forty-eight hours, are melted and cast into ingots. The process is said to be particularly suitable for the fine concentrates obtained by flotation, which are troublesome to treat in retorts.

At the Welland plant, Ontario, recently erected by the Weedon Mining Company, the solution of the zinc and electrolysis of the solution are performed in the same vat, the cathodes being enclosed in canvas bags. Other works adopt the arrangements at Anaconda.

It is proposed to use the method employed by the Anaconda Copper Company, described above, for the treatment of the complex zinc-lead sulphide ores which occur in large quantities in the Mount Read district of Tasmania. In these ores the metals are found in such an intimate state of fine division as to render concentration almost impossible. After much experiment, chemical treatment has been found to be the only feasible and economic method of dealing with such ores, and after trying several methods of wet extraction it is proposed to use the Anaconda method as stated. This has been rendered possible by the electric power scheme of the Tasmanian Government which has been in operation since May, 1915. The main water-storage basin is the Great Lake, and the present output is about 10,000 horse-power, but this can be very con-siderably increased in the future. The probable consumption of hydro-electric power in Tasmania in the near future for zinc ore reduction processes is estimated as 2,500 horse-power.<sup>1</sup> The electrolytic production of zinc is proposed by several companies.

<sup>&</sup>lt;sup>1</sup> "Tasmanian Hydro-electric Power and Chemical Industry," F. H. Campbell, Proceedings of the Society of Chemical Industry of Victoria, 1916, pp. 419-429.

In the Gillies process, the zinc sulphate is electrolysed between a rotating cylindrical zinc sheet as cathode and lead anodes, with a woollen diaphragm for separating the gases.

The bisulphate process is another wet method of zinc extraction which has been tried in several localities, including Tasmania, for the treatment of complex sulphide ores containing zinc. In this process the roasted ore is pulped with water and sulphur dioxide gas passed through the mass, resulting in the zinc passing into solution as the soluble bisulphite,  $ZnH_2(SO_3)_2$ .<sup>1</sup> This solution is pumped into another tank where the monosulphite of zinc is precipitated, and this yields the oxide on roasting in a muffle furnace.

The sulphur dioxide evolved at two stages in the above process is added to the roaster gases, which are in turn employed as the source of the sulphur dioxide used in the initial leaching process. A certain quantity of sulphate of zinc collects in the leaching solution, and this is periodically recovered by crystallisation.

The "French" process of zinc recovery, which is in operation at Silverton, British Columbia, has several points of interest. Roasted zinc blende is treated with a solution of sodium bisulphate (nitre cake) containing a small quantity of a manganese compound, usually manganese sulphate. After about an hour the solution has extracted almost the whole of the zinc, whilst the iron, lead and silver remain in the insoluble sludge.

The liquor from the first extraction is run on to a second charge of ore in order to neutralise its acidity, and when this has taken place the clear solution is run into vats and the zinc recovered electrolytically, using lead and zinc electrodes. Any manganese present is deposited on the lead as manganese dioxide, which is redissolved and used over again, whilst the zinc is deposited on the zinc electrode. As the zinc is electrolytically deposited, the sodium bisulphate is regenerated, and when all the zinc has been removed the solution is again ready for use and is employed in re-treating the charge of ore previously used to complete the neutralisation of the solution. It is stated that the process can be employed equally well for low or high grade ore, although in the former case the cost of treatment is somewhat higher.

In the opinion of W. R. Ingalls,<sup>2</sup> the electrolytic refining of <sup>1</sup> Bulletin of the Imperial Institute, 1916, vol. xiv, p. 69. <sup>2</sup> Loc. cit. zinc is only practicable where power is very cheap, or where other conditions are exceptionally favourable, such as a readily soluble ore, as at Anaconda, or one high in silver.

The crude zinc ore at Anaconda lends itself very successfully to treatment by the flotation process, which gives a high-grade concentrate. This is of such a nature that by roasting and leaching with weak sulphuric acid the percentage of zinc extracted as sulphate is unusually high.

This is not often the case with ordinary ores, which very frequently contain sensible quantities of iron and manganese which form troublesome compounds in roasting and lower the percentage of zinc recoverable by lixiviation.

The recovery of silver from zinc ores, which is only 65 per cent. in the distillation process, amounts to 90 or even 95 per cent. in the electrolytic process.

The concentrated ore at Anaconda contains 20 oz. of silver per ton.

The zinc produced is of high purity, and in view of the increasing demand for pure metal for alloying purposes the electrolytic methods of zinc extraction are receiving renewed attention, especially in connection with the recovery of the metal from by-products and residues, etc., containing zinc. The prospects of electrolytic zinc in relation to distillation methods of zinc extraction have been very ably dealt with by W. R. Ingalls in a recent paper on "Electrolytic Zinc,"<sup>1</sup> to which all interested in the subject are referred.

<sup>1</sup> W. R. Ingalls, "Electrolytic Zinc," Engineering and Mining Journal (New York), March 4th, 1916, vol. ci, pp. 425-428.

# CHAPTER VIII

#### THE PHYSICAL AND CHEMICAL PROPERTIES OF ZINC

ZINC is a bluish-white metal possessing a bright metallic lustre and is capable of taking a high polish. As usually met with in commerce and used, the metal is impure, and seldom contains more than 99 per cent. of zinc. Zinc in a chemically pure condition may be prepared by the electrolysis of a chemically pure solution of the sulphate or chloride, and if effected with scrupulous care in every particular will afford zinc of 99.998 per cent. purity. The pure metal is comparatively soft, being softer than copper, but harder than tin and silver.

The hardness of cast zinc measured by Brinell's method is 38.1, compared with copper 40.0, and silver 24.8.

Pure zinc is appreciably hardened by quenching in water after casting. The pure metal is malleable and may be rolled into thin sheets at the ordinary temperature, but commercial cast zinc is moderately hard and brittle at the ordinary temperature, a flat ingot, or cake, of the metal being fairly easily broken across under a blow from a heavy hammer. Although commercial zinc is very much less brittle than antimony or bismuth. the crystalline structure of the metal causes it to split and break up if hammered or rolled cold. The fracture exhibits large crystal faces of high metallic lustre, especially when the metal is free from iron. The appearance of the fracture is characteristic and affords an indication of the purity of the metal. The fracture is more largely crystalline the higher the temperature of casting is above the melting point of the metal. When bent, the cast metal emits a sound resembling the " cry of tin," but somewhat more feeble.

The commercial metal becomes malleable and ductile if heated

to a temperature of from 100° C. to 150° C., after which treatment it retains its malleability when cold sufficiently to admit of being rolled into thin sheet or drawn into wire. On a large scale, however, the metal is rolled hot. At a temperature above 205° C. zinc again becomes so brittle that it may be pulverised in an iron mortar. In common with other metals, zinc is hardened by mechanical treatment, such as rolling, and requires annealing at a low temperature to restore its malleability. It has been shown by T. K. Rose<sup>1</sup> that, in the case of pure sheet zinc 1.25 millimetres thick, softening is nearly completed in about half an hour at a temperature of 125° C.

Zinc is less tenacious than most metals in common use, its tenacity, according to Karmarsch, being 2,809 lb. per square inch when cast, and between 18,703 lb. and 22,188 lb. when in sheets or wire.

Measurements of the tensile strength of rolled zinc have been made by H. F. Moore,<sup>2</sup> which show that zinc, either in the cast or rolled state, has no definite yielding point. The breaking load of thin rolled zinc (not more than 0.05 inch thick) was found by Moore to be about 24,000 lb. per square inch, and its tensional modulus of elasticity II,500,000 lb. per square inch. Rolled zinc is somewhat stronger in tension across than with the grain. The stress developed in punching or shearing the rolled plates is about 40 per cent. of that developed with mild steel plates.

The sheets are more ductile with the grain than across it. Results obtained by T. K. Rose<sup>3</sup> show that zinc hardened by rolling is in an unstable condition at the ordinary temperature and undergoes a gradual change to the soft state. Thus the scleroscope hardness of rolled zinc was found to be 36, and after ninety-seven days the hardness had fallen to 31.0. Zinc may be granulated by pouring the molten metal into water. In hot water it is obtained in the form of small globules, known as bean-shot, and in cold water flakes are produced, known as feathered-shot metal. Both these forms of granulated zinc are prepared commercially.

The density, or specific gravity, of cast zinc ranges from 6.9 to 7.2, according to the temperature at which it has been

<sup>&</sup>lt;sup>1</sup> Journal of the Institute of Metals, 1912, vol. viii, p. 114.

<sup>&</sup>lt;sup>2</sup> University of Illinois Bulletin, 1911, vol. ix, No. 9. (Abstract Journal of the Institute of Metals, 1915, No. 2, vol. xiv, p. 230.)

<sup>&</sup>lt;sup>3</sup> Journal of the Institute of Metals, 1912, No. 2, vol. viii, pp. 86-114.

cast and the manner in which it has been cooled. By rolling the metal its specific gravity is increased to about 7.25.

The electrical conductivity of zinc is 25.6 to 29.9, according to the determinations of several observers, and its thermal conductivity 28.1, compared in both cases with silver as 100.

The atomic weight of zinc is 65.37 (taking O = 16), and its symbol is Zn.

Zinc melts at a comparatively low temperature, its melting point being 419° C.; it boils at 950° C., the vapour burning in air with a characteristic brilliant bluish-green flame, and the production of zinc oxide, a soft, white, flocculent substance resembling wool; and formerly known as *philosopher's wool*, or "flowers of zinc." According to Ingalls, zinc burns in the air at a temperature as low as 500° C. It can be distilled in quantity at a bright red heat, and on cooling condenses in globules which coalesce, when a reducing atmosphere is maintained.

When it passes from the cold solid to the molten condition zinc increases in volume II·I per cent. It contracts but slightly on cooling from the molten state, and is thus well adapted for castings. The molten metal retains a small quantity of zinc oxide, which separates on solidification, presenting very thick crystal boundaries when examined under the microscope.

Zinc expands  $\frac{1}{340}$  th of its length by heating from 0° C. to 100° C.

The metal is not affected by pure dry air or by oxygen at the ordinary temperature, but under ordinary moist atmospheric conditions it gradually acquires a coating of the greyish-white basic carbonate which protects the metal from further corrosion. In consequence of this property, zinc is used in the form of sheets for roofing purposes, and is also employed as a protective covering for iron, which when thus coated is said to be *galvanised*, a term that is somewhat misleading, since the iron is not ordinarily coated by electrical deposition, but by dipping the iron into a bath of molten zinc. The industrial value of zinc is largely due to this protective property.

Pure zinc is scarcely acted upon by pure sulphuric or hydrochloric acid, either dilute or strong. The presence of small quantities of impurities, however, determines the rate of solution of the metal, hence ordinary commercial zinc is readily attacked by these acids with rapid evolution of hydrogen, and on this account the metal is used as the positive element in electric batteries. When zinc is brought into contact with mercury, zinc amalgams are formed which are only very slowly acted upon by dilute sulphuric acid; therefore, by the superficial amalgamation of the zinc plates used for electric batteries, the same result is obtained as though the zinc were perfectly pure, and no solution of zinc takes place until the electric circuit is closed. Amalgamation protects zinc from corrosion by acids, because the discharge potential of hydrogen on mercury exceeds the potential of zinc.

Sulphuric acid dissolves zinc appreciably more slowly than hydrochloric acid with an equal concentration of hydrogen ions.

Owing to the differences in the crystalline structure of the metal, cast zinc is less easily acted upon than rolled zinc by dilute acids. The dark grey residue obtained on treating the commercial metal with acids consists chiefly of lead.

Both pure and commercial zinc are dissolved readily by alkalis. Water has no action on zinc at the ordinary temperature, if air is excluded, but at a red heat the metal readily decomposes the vapour of water and is converted into oxide.

Carbon dioxide very readily oxidises zinc vapour with the production of carbon monoxide and zinc oxide. This reaction, as previously pointed out, is of considerable importance as it constitutes a decisive factor in the metallurgy of zinc, and confines within very narrow limits the methods that are applicable, on a commercial scale, to the extraction of the metal from its ores.

Zinc is strongly electro-positive and readily precipitates most other metals from their solutions. In this connection it finds industrial application; e.g. it is in extensive use for precipitating gold from cyanide solutions in the cyanide process of gold extraction.

Zinc unites with most of the common metals to form a number of useful alloys, the most important of which are the various forms of brass. The zinc alloys, and also a number of zinc compounds, of value in the industries, are discussed under the "Industrial Applications of Zinc" (see p. 161).

# The Micro-structure of Zinc

The evidence afforded by the microscope, in relation to the constitution of metals and alloys, has been of such value that the systematic study of the micro-structure of commercial samples of zinc and its alloys is now very generally undertaken. In particular, the systematic study of brass and of nickel silver as revealed by the microscope has claimed a considerable amount of attention in recent years.

The rapid growth of this new science of metallography, and the attention paid to it by both manufacturers and users of metals, is a cause for much satisfaction, as it evidently indicates that those connected with the British metal industries are beginning to recognise the fact that any advance in purely scientific knowledge of metals is capable of being turned to practical advantage.

The chief points ascertainable by the use of the microscope are the crystalline state of the metal or alloy, and changes in the general structure due to varying mechanical or heat treatment, and the constitution of the material, that is to say, the differentiation of the various constituents which enter into the composition of the alloys. This is one of the most important points connected with the modern study of alloys, and much valuable information has now been obtained by this method of investigation.

As regards crystalline structure, attention may be directed to the distinction between the grains of which a mass of metal is usually composed and the crystallites which compose each grain, the latter constituting the true crystalline structure. In each grain the crystallites are arranged in a definite direction or orientation. When, therefore, the surface of any pure metal, after having been carefully polished, is lightly etched with a weak acid or other reagent and examined under the microscope, it is seen to be composed of a number of separate grains, irregular in size and shape. If the etching be made deeper it is found that the grains, besides differing in size, differ also in texture, reflecting at different angles light thrown upon them.

Examination of the strongly etched surface under a higher power shows that this difference in texture is due to a number of small facets in each grain. The facets are oriented, but in any one grain they are similarly oriented, so that the general surface of the grain reflects light in a particular direction. Each of these grains has the uniformity of internal structure characteristic of a crystal and is, in fact, a crystal. With this fundamental fact established, the cause of the behaviour of metals under different conditions, under strain, for example, can be explained, but much remains yet to be investigated. In particular, no completely satisfactory explanation of the manner in which the individual crystalline grains are cemented together has yet been obtained.

Well-defined or idiomorphic crystals are seldom found in the structure of cast metals, while crystallites or the incipient forms of crystals are predominant. On annealing, however, this crystallitic structure is replaced by a well-defined crystalline structure.

Various etching reagents are in use for developing the structure of zinc and its alloys. For etching the surface of zinc Timofeef<sup>1</sup> recommends a mixture of 94 per cent. nitric acid and 6 per cent. chromic acid, a few drops of this mixture being added to 50 or 100 cubic centimetres of water before use. This reagent is also recommended by Desch, and has been found satisfactory in practice.

Iodine is found by Gulliver to be most suitable for alloys rich in zinc or cadmium.<sup>3</sup> He uses a solution of I part iodine and 3 parts potassium iodide in IO parts of water.

Caustic potash and caustic soda are used for zinc and aluminium and alloys rich in these metals. When caustic soda is used for etching alloys of aluminium with zinc, a black deposit is often left on the etched surface. This can be very satisfactorily removed by dipping the specimen in a solution of chromic acid in water.

The strength of the caustic soda reagent varies from 5 to 20 per cent. A 10 per cent. solution of chromic acid etches zinc, cadmium and many alloys of these metals, whilst a highly concentrated solution of chromic acid is, according to Czochralski,<sup>3</sup> suitable for developing the internal crystalline structure of zinc.

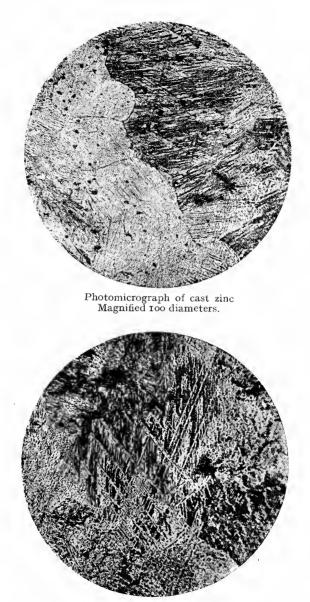
The micro-structure of pure cast zinc consists of comparatively large grains, often showing a cross-hatching upon their surfaces, presenting a structure analogous to that of martensitic steel. A photomicrograph of cast zinc, etched with very dilute nitric acid, and magnified 100 diameters, is shown in Plate 1.<sup>4</sup> Another

<sup>&</sup>lt;sup>1</sup> "Revue de Métallurgie," 1914, No. 1, p. 127.

<sup>&</sup>lt;sup>2</sup> O. F. Hudson, "Etching Reagents," Journal of the Institute of Metals, 1915, No. 1, vol. xiii, p. 193.

<sup>&</sup>lt;sup>3</sup> "Stahl und Eisen," 1915, vol. xxv, pp. 1073, 1129. Abstract Journal of the Institute of Metals, 1916, No. 2, vol. xvi, p. 245.

<sup>&</sup>lt;sup>4</sup> Photomicrographs taken for the author by Dr. F. C. Thompson, University of Sheffield.



Photomicrograph of cast zinc (showing twinning). Magnified 100 diameters

photomicrograph of the same metal, treated as before, is also shown in Plate r. In this latter case the structure consists of allotriomorphic crystals with twinning, which is of somewhat rare occurrence in metals in the cast state.

When the zinc is contaminated with zinc oxide, which is usually the case with commercial samples, the oxide tends to separate at the crystal boundaries, giving rise to very thick boundary lines.

The changes in structure of hard worked zinc on annealing are discussed by G. Timofeef. Cast specimens of zinc were prepared and strained in compression. The micro-structure of zinc crushed in a vice becomes homogeneous, no crystals being visible under very high magnifications. The hardness increases considerably. Recrystallisation takes place, however, very readily on annealing the metal, a very slight rise in temperature effecting a noticeable change in the micro-structure of the strained metal. The etching of the samples was effected with Timofeef's reagent given above. The strained specimens were annealed at different temperatures ranging from  $65^{\circ}$  C. to  $360^{\circ}$  C.

The photomicrographs showed that the average size of the crystal grain in the annealed specimens increases uniformly with the annealing temperature, the hardness suffering a corresponding decrease in value, until it finally reaches the same figure as that found for the cast metal. It was found in all cases that the size of the grains was greater at the edges than in the middle of the specimens; this is ascribed to the greater amount of plastic strain at the edges of the specimens during deformation by compression.

It is concluded that the velocity of recrystallisation depends both upon the temperature of annealing and upon the severity of plastic strain; the final size of the crystalline grains when annealing at a given temperature is limited by the duration of heating. Under slight shock the large individual crystals composing cast zinc became striated, this effect being produced even by removing the ingots from moulds, if special care is not taken.

The micro-structure of zinc containing lead indicates that at the freezing point of zinc the still molten lead is rejected and forms minute globules occupying often the cleavage cracks caused by the contraction of the crystalline zinc during solidification. This separation of lead is well shown in Plate 2, which in the lead appears as isolated dots within the zinc crystals. The cast zinc contained about 3 per cent. of lead, and the structure was developed by etching with very dilute hydrochloric acid with the addition of a few drops of a solution of zinc chloride. The magnification is 100 diameters.

Iron is a frequent constituent of commercial zinc, and when present above 0.1 per cent. it forms distinct crystallites which are readily discernible under the microscope, and, as already stated, are doubtless the cause of the light specks on the crystal faces of fractured spelter. Hard zinc, containing about 10 per cent. of iron, presents a characteristic structure in which the crystals are well defined even at a low magnification of about 30 diameters.

The microscope affords a very ready means of controlling the annealing process for brass and other zinc alloys, and has been adopted for that purpose in several large works. After every stage of the process samples are taken, rapidly polished, etched and examined under the microscope. From the size of the crystals it is easy to determine whether the alloy has been insufficiently, correctly, or over annealed.

The accompanying photomicrographs of brass, containing 60 per cent. of copper and 40 per cent. of zinc, are given as illustrations of the study of the constitution of brasses by means of the microscope.

Plate 3 represents the brass (copper 70, zinc 30) as cast, while Plate 4 shows the appearance of the metal after annealing for one hour at 750° C. The magnification in each case is 80 diameters.

The etching-agent was a 10 per cent. solution of ammonium persulphate.

For further examples of the micro-structure of brass and other alloys containing zinc reference must be made to the researches on the subject that have been published in the Proceedings of the scientific societies, notably in the *Journal of the Institute of Metals*, and several of which have been mentioned in the Bibliography appended.



Photomicrograph of cast zinc with 3 % of lead. Magnified 100 diameters.

PLATE 2.



Brass (70 % copper, 30 % zinc) as cast; showing cored structure. Magnified 80 diameters. Etched with 10 % solution of ammonium persulphate.

> Photomicrograph by Dr. F. C. Thompson, University of Sheffield.

> > Plate 3.



Brass (70 % copper, 30 % zinc) after annealing for one hour at 750° C.; showing crystalline structure. Magnified 80 diameters. Etched with 10 % solution of ammonium persulphate.

Photomicrograph by Dr. F. C. Thompson, University of Sheffield.

PLATE 4.

## Impurities in Commercial Zinc

Owing to the fact that zinc possesses so powerful an alloying affinity for other metals, and even metalloids, *e.g.*, arsenic, the commercial metal produced by distillation is invariably contaminated with impurities, the amount of which varies according to the composition of the ore from which the spelter is produced.

The most frequent impurities in spelter are lead, iron, cadmium and arsenic. From the table of typical analyses given on p. 149 it will be seen that the chief impurities to be guarded against are lead and iron.

The variations in the lead and iron content in different brands of spelter examined by R. T. Rolfe<sup>1</sup> during the years 1913-1916 were as follows:

Brand of	Spelt	er.	Lead per cent.	Iron per cent.	
Crown De Boom Nouvelle Montagn Revil S.S Ste. de Boom Vieille Montagne Vivian & Co.	e    	· · · · · · · · ·	· · · · · · · · · · ·	1.52 0.31 0.94 0.46-1.73 0.32-3.43 1.65-2.03 1.47-1.49 0.83-1.32	0.08 trace 0.03 0.07-0.19 trace trace 0.04-0.07 0.08-0.12

Lead.—The lead does not usually exceed 2 per cent., although some spelters are placed on the market containing as much as 3 per cent. It is usual, however, to refine such impure metal before marketing, since, as already stated, the quantity of lead present very largely determines the market value of the spelter.

In spelter intended for rolling, a small percentage of lead is desirable, and up to 10 per cent. it has no injurious effects on the malleability or ductility of the metal.

When, however, the spelter has to be used for making brass which has to undergo severe mechanical treatment, as, for example, the manufacture of cartridge cases, the presence of lead exceeding 0.1 per cent. is very undesirable, the metal being often somewhat brittle and liable to crack. When present in quantities greater than 0.7 per cent., lead tends to produce bad cracking in spelter castings.

<sup>1</sup> Journal of the Institute of Metals, 1916, vol. xvi, p. 201.

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Any cheap and readily applicable method for the elimination of lead from spelter, short of redistillation, would, in the opinion of Moulden, find both world-wide application and substantial remuneration.

*Iron.*—Iron is a very frequent impurity, the amount passing into the spelter depending more on the method of smelting than on the ore employed.

When over  $o \cdot I$  per cent., its presence is indicated by the grey appearance, and by the presence of a number of black specks (crystallites) on the crystal faces of the fractured spelter, while the pure metal exhibits clear, brilliant crystal faces on fracture.

The zinc may be freed from this impurity by redistillation, the use of iron tools and appliances being avoided. The effects of iron are to increase the hardness and brittleness of zinc and reduce its malleability, but when the refining by liquation has been properly conducted there is insufficient present to affect these properties.

For spelter intended for the manufacture of brass 0.05 per cent. of iron is often specified as the limit, but less than this amount is preferable for brass of high ductility and malleability.

*Cadmium.*—Cadmium, being more volatile than zinc, is more difficult to condense, and is rarely present in spelter in injurious proportions.

Spelter may, however, contain as much as 2  $\circ$  per cent. of cadmium, but usually the quantity is under  $\circ 2$  per cent. Spelter free from cadmium can only be obtained by single smelting when the ore is free from cadmium, but by redistilling common spelter with proper control of the temperature, and separating the first distillate, a high-grade spelter, low in cadmium, is easily produced.

Cadmium has a pronounced hardening effect on spelter and tends to increase its brittleness, but its effect on zinc to be used for the production of alloys requires further investigation. As the result of practical experience many metallurgists consider that cadmium up to 0.5 per cent. has no injurious effect on zinc used in the manufacture of cartridge brass, nickel silver, and similar alloys.

The specification of military engineers for high-grade spelter for the production of cartridge brass permits a maximum of only 0.15 per cent. of cadmium.

Season cracking in brass, which was formerly attributed solely to cadmium, is now recognised to be the result of internal strains due to improper heat treatment or the entire lack of heat treatment. On the other hand, cadmium if present beyond 0.5 per cent. is considered to be injurious when the spelter is used for sheet rolling, for galvanising, and for making slush (ornamental) castings. Its presence in galvanising is very important, as brittleness due to cadmium causes the coating to peel off. This is of particular importance in galvanised wires for telephone and telegraph purposes, which are sharply bent in making splices.

Cadmium has a strong tendency to make castings crack. In brass cadmium tends to act like lead, and is also said to make the metal more sensitive to heat treatment. The amount present in brass is, however, seldom large, since it readily volatilises during melting.

Arsenic, Antimony, Copper, Sulphur and Carbon.—These elements are seldom present in sufficient quantities in spelter to affect its properties for the uses for which the metal is usually employed. Arsenic, however, should be absent in zinc used for generating hydrogen for use in lead burning, or autogenous welding, otherwise it is often impossible to burn a strong seam. It should also be absent in zinc intended for the precipitation of gold in the cyanide process, as in treating the precipitate with acid arseniuretted hydrogen is given off, and this has resulted in several fatal accidents.

Tin and Aluminium should always be looked for in remelted spelter. Tin tends to make zinc very hard and brittle in rolling. Some brands of remelted spelter contain aluminium, usually to the extent of about 0.3 per cent.

Small quantities of copper are not infrequently present in remelted spelter.

# CHAPTER IX

#### THE MARKETING OF ZINC

## Grades of Commercial Zinc

THE quality of commercial zinc varies considerably according to the method of production, but in many cases the sole practical difference between ordinary commercial spelter and the much more valuable fine-zinc is represented by the lead content. For some industrial uses zinc is required in a state of fairly high purity, consequently there is a good demand for high-grade metal.

The brands of zinc produced by remelting scrap metal, &c., usually contain impurities and are of inferior quality.

The slab zinc is marketed under various names, which are used by the different smelting companies to denote their products, the quality of which is known to the users of zinc.

A large number of brands of spelter are made on the Continent. Many of the works make two or three different brands, varying in quality and price mainly according to the lead contents, but in some cases dependent upon whether the metal is higher or lower in iron. The grading of commercial zinc according to the amount of impurity, especially lead, is most desirable, and, as shown below, has been generally adopted in America in recent years. In this country, however, a hard and fast classification does not appear to obtain, and what are described as good ordinary brands show a very large variation in the proportion of lead. Furthermore, different consignments of spelter of the same brand will often vary in this manner to an undesirable degree.

In good ordinary brands (G.O.B.) of British spelter the lead usually varies from 0.8 to 1.8 per cent. and the iron from 0.02 to

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0.04 per cent. In Silesian unrefined spelter, as tapped in hand ladles, the lead is usually higher, reaching over 2 per cent. In some brands of American high-grade zinc lead is absent or does not exceed 0.02 and the iron 0.01 to 0.02 per cent. The brands of electrolytic zinc seldom show higher purity than is obtainable by modern fire refining. The purity in both cases is usually guaranteed 99.95 per cent. of zinc.

The following analyses of British, Continental and American brands of spelter may be taken as typical:--

Brand.	Zinc. Per cent.	Lead. Per cent.	Iron. Per cent.	Cad- mium. Per cent.	Tin. Per cent.	Copper. Per cent.
Central Zinc Co. (British) <sup>1</sup>	98.642	I·205	0.06	0.080	_	0.004
V.M.G. (Belgium) <sup>2</sup>	99.05	0.66	0.26		0.03	
Vieille Montagne (Belgium) <sup>2</sup>	97.89	2.00	0.04	0.07		l
Freiberg (Saxony) <sup>2</sup>	98.84	1.03	0.04	0.02	0.07	
Lazyhutte (Upper Silesia) <sup>2</sup>	97.85	1.12	0.02	0.017		
Lipine Electrolytic (Upper	51-5			/		
Silesia) <sup>2</sup>	99.905	0.06	0.01	0.002	0.02	
Font-d'art (France) <sup>3</sup>	99.718	0.135	0.20	0.123		trace
Scrap8	96.447	2.05	0.03	0.003	1.41	0.06
561ap	95 447	2.05	5 05	0.003	- 4-	

ANALYSES OF COMMERCIAL ZINC.

The virgin spelter produced by the Central Zinc Company, at Seaton Carew, Durham, is from Broken Hill ore.

The American Society for Testing Materials suggested in 1911 the following four grades for commercial spelter.

G <b>ra</b> de.		Lead. Per cent.	Iron. Per cent.	Copper. Per cent.	Total not over per cent.
<ul> <li>A. High grade</li> <li>B. Intermediate</li> <li>C. Brass special</li> <li>D. Prime Western</li> </ul>	•••	0.07 0.20 0.75 1.50	0.03 0.03 0.04 0.08	0.05 0.05 0.75	0·10 0·50 1·20

<sup>1</sup> Moulden, Journal of Royal Society of Arts, 1916, vol. lxiv, p. 512.

<sup>2</sup> Primrose, Journal of Institute of Metals, 1909, vol. ii, p. 234.

<sup>3</sup> Jones, Journal of American Institute of Metals, 1915.

#### THE ZINC INDUSTRY

The figures represent the maximum percentage of impurities allowable. This classification corresponds substantially with the understanding among American zinc smelters.

The following table gives the analysis of typical commercial samples of the various grades of American spelter <sup>1</sup>:—

Grade	•		Zinc. Per cent.	Lead. Per cent.	Iron. Per cent.	Cadmium. Per cent.
High grade	••		99•960	•010	·026	•040
	••	••	99.945	•041	014	
yy yy Tadaana adlada	••	• •	99.951	·035	•014	
Intermediate	••	••	<b>99-8</b> 96	•095	•009	
	••	••	99.793	•190	•017	
_ "	••	••	99•746	·I23	·011	·120
Brass special	••	••	99.631	•343	•026	
		• •	99.213	•474	·013	
,, ,, ,,	••	••	99 <b>·0</b> 36	·68o	•0I0	•274
Prime Western	• •		99.045	·870	•062	.023
., .,			98.253	•644	·013	1.000
	• •		98.641	1.270	.010	•079
Willemite (East	ern l	 Penn-	98.503	1.448	·024	•024
sylvania) <sup>2</sup>	••		99 <b>•9</b> 55	•039	oo3 and copper oo1	•001 and coppe •002

The "Prime Western" brand corresponds with "good ordinary brands" in European quotations and includes the bulk of American spelter.

The grade produced in largest amount in America is "Prime Western," a considerable part of which is used for galvanising iron and steel wire and sheet. "Brass special" is used chiefly in the manufacture of brass. The price of "high-grade" spelter is usually 2 to 4 cents per lb. more than that of "Prime Western." The "high-grade" and "intermediate spelters" are made by only a few smelters, but the "brass special" and "Prime Western" are made by many concerns.

Sampling Zinc.—Slabs of spelter as supplied by the smelter are not of exactly uniform composition, as the kettle into which the metal is received from the furnace holds a relatively small quantity, and the impurities passing over with the zinc vary in

<sup>1</sup> G. C. Stone, Transactions of the American Institute of Metals, 1915, vol. ix.

<sup>2</sup> J. L. Jones, ibid.

amount in different parts of the furnace, according to the temperature of the retort. To ensure uniformity as far as possible, the zinc should be tapped into large ladles or remelted in large pots or furnaces before being cast into slabs for delivery.

Segregation of the impurities, however, invariably takes place, and slabs of commercial zinc are rarely uniform in composition. Under these conditions the sampling of the slabs is a matter of considerable importance, although it does not always receive the attention it deserves.

One slab out of every ten should be taken for sampling to secure a trustworthy average of the shipment or consignment, but this practice is not always carried out. American brassmakers follow a time-honoured practice of sampling a carload (about 50,000 lb. of spelter in 820 to 960 slabs) by drawing 10 slabs at random, and that practice has recently received the endorsement of the American Society of Testing Materials.

The sample for analysis is taken from the selected slabs either by breaking a small piece off one corner of each slab or by drilling right through each slab.

The latter method is the more satisfactory, provided proper precautions are taken to prevent contamination of the sample with iron from the drill. A twist drill, about  $\frac{3}{8}$  inch, is very suitable for the purpose. It must be kept sharp and be fed slowly enough to enable it to clear itself of all drillings. If this is not done, the drillings are liable to pick up iron from the drill in such a firmly adhering form that removal by means of the magnet or otherwise is out of the question. Sampling by sawing the slab completely through with a band saw, as is frequently done in sampling pigs of lead, has been adopted in a few cases with satisfactory results.

# The Price of Zinc

When viewed over a considerable period of years, the market value of spelter has, not unnaturally, fluctuated considerably. When first produced it realised a high price, which rapidly fell as production increased and no new output for its consumption opened out.

In reviewing the price of zinc Moulden points out that in 1807<sup>1</sup>

<sup>1</sup> The prices quoted, 1807 to 1850, are based upon figures as given by Liebig: "Zink und Cadmium," Leipzig, 1913 (per J. C. Moulden).

it was about £40 per ton, rose in 1808 to £84 per ton, and then fell steadily as production overtook demand, until in 1820 it stood at no more than £11.

The extension of sheet rolling caused the price to rise until in 1825 it reached £30; it fell again as production increased, and between 1830 and 1836 fluctuated between £10 and £19. It again fell to £10 in Breslau (the Silesian centre) in 1848. In 1850 it was quoted at about £16, and from that time onward to 1913 the yearly average fluctuated between £13 19s. 11d. (the lowest touched in 1885) and £27 1s. 5d. in 1906.

Moulden remarks that the general tendency of late years has been towards a distinctly higher average level. For a very long time low wages and easily won and treated ores kept the price low. As wages increased and difficulties of treatment arose the improvements in metallurgical efficiency and extraction kept pace up to a certain point and compensated the producer. Beyond this point there was bound to be a rise in average value, and this is clearly reflected in the fact that only twice since 1898 has the average price been below  $\pounds 20$ , and never since the close of 1902. Prior to the war industrial conditions had reached such a point that, broadly viewed, a  $\pounds 20$  market was considered by smelters to be unremunerative and distinctly unprofitable in particular for those concerns which did not themselves possess mines.

The establishment of the Zinc Conventions (see p. 155) and the German control of Australian concentrates, not unnaturally, had some influence in regulating the price of spelter.

"The Metallgesellschaft, acting on behalf of the German Group, purchased for a number of years the whole supply of Australian zinc concentrates, and the price was regulated by the average of the mean daily quotations made on the London Metal Exchange. The Metallgesellschaft, through its Australian connection, the Australian Metal Company, and Hirsch & Company, through their Australian representative, arranged the contract with the Broken Hill Groups. "The contract was made so that if the price of spelter rose

"The contract was made so that if the price of spelter rose above  $f_{22}$  or  $f_{23}$  a ton, any excess above that price was divided equally between the buyer and the seller. That contract having been signed, the European Spelter Convention was formed about the middle of January, 1909. Spelter at that time was  $f_{21}$  Ios. a ton, and it is now common knowledge that it was forced up to more than  $f_{27}$  a ton. The higher price brought a remarkable increase in production, so that the price, after touching more than  $f_{27}$  a ton in 1911 and 1912, fell during the first half of 1913 to  $f_{22}$  a ton, and during July and August of the same year to about  $f_{20}$  IOS. a ton."<sup>1</sup> Thus the successful negotiations and contracts for the Australian was a mere question of  $f_{s}$  s. d. or who would pay the highest price.

Owing to the conditions that prevailed consequent upon the outbreak of war, the selling price of spelter appreciated to more than five times its pre-war figure. During 1915 the price of the metal was subject to more violent fluctuations than have been recorded during the past fifty years.

THE HIGHEST, LOWEST, AND AVERAGE PRICE PER TON OF COMMERCIAL METALLIC ZINC IN THE LONDON MARKET FROM THE YEAR 1900 TO 1917.

Year.			English spelter.	Foreign spelter.	
	Highest.	Lowest.	Average.	Average.	
1900          1901          1902          1903          1904          1905          1906          1907          1908          1909          1910          1911          1913          1913          1915          1917	$ \begin{array}{c} f & s. & d. \\ 22 & 15 & 0 \\ 18 & 18 & 9 \\ 19 & 17 & 6 \\ 23 & 18 & 9 \\ 25 & 10 & 0 \\ 29 & 2 & 6 \\ 29 & 10 & 0 \\ 28 & 2 & 6 \\ 21 & 17 & 6 \\ 23 & 6 & 3 \\ 24 & 5 & 6 \\ 27 & 17 & 6 \\ 27 & 12 & 6 \\ 34 & 0 & 0 \\ 120 & 0 & 0 \\ 120 & 0 & 0 \\ 110 & 0 & 0 \\ 57 & 0 & 0 \end{array} $	$ \begin{array}{c} \pounds & s. & d. \\ 18 & 10 & 0 \\ 16 & 0 & 0 \\ 16 & 7 & 6 \\ 19 & 15 & 0 \\ 21 & 2 & 6 \\ 23 & 5 & 0 \\ 24 & 0 & 0 \\ 19 & 10 & 0 \\ 19 & 10 & 0 \\ 19 & 10 & 0 \\ 18 & 0 & 0 \\ 21 & 1 & 2 \\ 6 & 0 \\ 21 & 1 & 2 \\ 6 & 25 & 0 \\ 22 & 17 & 6 \\ 25 & 0 & 0 \\ 21 & 6 \\ 3 & 28 & 0 \\ 44 & 0 & 0 \\ 44 & 0 & 0 \\ \end{array} $	£ s. d. 20 16 0 17 14 5 19 3 8 21 12 0 23 2 11 26 0 0 27 12 4 24 11 1 21 0 11 22 16 6 23 19 0 25 3 9 26 3 4 22 14 3 Average	$ \begin{array}{c} \pounds & s. & d. \\ 20 & 13 & 5 \\ 17 & 7 & 6 \\ 18 & 14 & 8 \\ 21 & 4 & 8 \\ 22 & 18 & 0 \\ 25 & 15 & 2 \\ 27 & 8 & 0 \\ 26 & 17 & 1 \\ 22 & 13 & 0 \\ 23 & 12 & 0 \\ 25 & 16 & 7 \\ 27 & 4 & 2 \\ 23 & 15 & 6 \\ \pounds 66 & 13 & 8 \end{array} $	

It rose gradually from  $\pounds 28$  per ton in January of that year to  $\pounds 120$  in June; then a reaction occurred, and by August the price had fallen to  $\pounds 55$  a ton. Thence up to November there was

1 H. Kaye, Journal of the Institute of Metals, 1916, vol. xvi, p. 186.

another increase until the price was again more than  $f_{100}$ . In 1916 the highest price reached was  $f_{110}$ , and the lowest  $f_{44}$ , while in 1917 the price rose to  $f_{57}$  and went as low as  $f_{44}$ . The year closed with zinc at about  $f_{52}$  per ton.

The yearly and monthly average prices of spelter for the ten years prior to the war are given in the table on p. 153.

In normal times the prices of metals reflect, in a large measure, the relation between production and consumption, but for some time past such cannot be said to be the case, as the metal industry is now controlled by the Government, almost all the available supply being devoted to the purposes of war, the ordinary trade requirements having, naturally, to be left unfilled.

## The World's Zinc Markets

London is the principal European zinc market, the price of the metal being quoted in  $f_{\rm s}$  s. d., according to the prevailing prices for G.O.B. ("Good ordinary brands" or "Good ordinaries"), and a slightly higher quotation for "Specials," the purer quality of zinc. As previously stated, many of the smelters, both in this country and abroad, make two or three different brands of zinc, varying in quality mainly according to the lead contents, but in some cases dependent on the iron content. They are sold at various prices, the better grades of metal naturally commanding higher prices. British spelter is usually quoted under the heads of "Ordinary brands," "Special brands," and "English Swansea."

The several selling centres for zinc in the German Empire are Breslau, Cologne, and Frankfort-on-Main. The price is always quoted in marks per ton, the difference in price between each brand being usually I or 2 marks.

The American zinc market is entirely independent of that of the rest of the world, as, under normal conditions, America is not favourably situated to compete with the British and Continental markets. The conditions relating to the marketing of zinc in America have been summarised recently by C. H. Fulton<sup>1</sup> as follows:—

<sup>1</sup> Technical Paper 83, Bureau of Mines, Washington, 1915, p. 38.

"The main market or basing point for spelter is St. Louis, Missouri, for the reason that the great zinc fields and a large number of the smelting plants for zinc are situated not far from St. Louis. However, the large consumption of spelter is at places between St. Louis and New York, and it is sold in New York on a St. Louis basis, the quotations being given in cents per lb. The New York price is the St. Louis price plus 15 cents per 100 lb., which is the freight rate on spelter from St. Louis to New York. The American market is in part independent of the European market, because spelter is protected by an import duty of 15 per cent. and zinc in ore by a duty of 10 per cent. ad valorem.

"In the marketing of zinc, it is customary for the producer to sell direct to the manufacturer. This policy, however, in view of the large number of producers, is not nearly so closely followed as in the selling of copper, and some of the producers, particularly the smaller ones, sell to anyone who cares to purchase. This condition of course gives rise to more speculation in zinc than in copper. The real spelter market is established by the private transactions of producer and consumer, and any information as to the state of the market can come only from them. The facilities for exchanging information in the spelter market are not as good as those in the copper market, and hence transactions between producer and manufacturer often show considerable difference in price." The four brands of spelter on the American market, with their names and permissible proportions of impurities, have been given on p. 149.

# The Spelter Convention

Prior to the outbreak of war the spelter market was very largely controlled by the Spelter Convention, an association of zinc smelters formed in 1909 and elaborated in 1910. Separate syndicates were formed for each zinc-producing country, and included all the German, most of the Austrian, Belgian and French, and many of the British smelters. The Convention consisted of three groups:--

Group A, known as the Verband, or German Syndicate, com-

prised the associated German and Belgian makers, whose output was disposed of by a joint selling office.

Group B comprised certain Belgian and French producers.

Group C comprised the British producers.

The two latter groups constituted the International Spelter Syndicate, which on December 18th, 1913, was, with slight changes, renewed on the old conditions until April 30th, 1916. The German Syndicate was also prolonged until the same date.

The object of the Convention was to control output by fixing, within certain limits, the individual production of its members, and to ensure a uniform mode of selling, and, if the market showed that the demand was not keeping pace with the output, to restrict the latter.

On the Continent, the sale of the metal was in the hands of the leading trading companies in metals and minerals, who, jointly with the producers, fixed the selling prices and the quantities to be produced by each works. Over-production above the quantities fixed by the board of management was subject to heavy penalties. The total of the amounts realised, after deduction of selling and administration expenses, was distributed amongst the various works in accordance with the deliveries made by them, and in taking into consideration certain geographical positions and superior qualities of spelter produced, various premiums were admitted. The smelters with their own mines ("Erzhuetten"), on the other hand, paid a certain amount for each ton of ore produced and treated by them to make up for the advantage they had against the "Lohnhuetten," or customs works, who bought their ore in the market.<sup>1</sup>

Restriction of output came into force when the average price of spelter in the London market had remained at  $f_{22}$  or under for two months, and when the unsold stocks, which were taken quarterly, amounted to 50,000 tons.

The British and French smelters were bound to a joint restriction of output in certain circumstances, but they had more liberty of action than the other members, being free from selling restrictions. The German smelters were under the most stringent rules as regards production, prices and agencies through which sales could be made.

<sup>1</sup> J. Gilbert, Mining Journal, London, 1916, vol. cxiv, p. 497.

American smelters were not included in the Convention, as the home consumption at that time equalled the production, and it was therefore unlikely that they could influence the European market.

Pursuant to the above provisions the International Syndicate on May 26th, 1913, reduced prices by 50s. per ton, and the London quotation went down to  $\pounds 23$ . On October 1st, 1913, the Convention ordered a reduction in output of 8 per cent.

"On the whole," according to J. Gilbert, 1 " the Spelter Syndicate may be said to have served the interests of European producers to some considerable extent by regulating the uniformity of the supply, which has permitted a steady progress of the industry, with fairly uniform remuneration of capital and labour, and without unduly exposing it to the inveterate risk of speculation, which very frequently most radically interferes with the interests of both producers and consumers of certain commodities. Unfortunately, however, so far as British interests are concerned, one all-important feature has been overlooked, and that is the fact that, whilst British consumers of spelter absorb about 40 per cent. of the European production, the British production of spelter hardly exceeds 10 to 12 per cent. of the European output."

### The Production and Consumption of Zinc

*Production.*—Owing to the complications introduced by primary and secondary and redistilled hard spelter, &c., it is very difficult to ascertain with accuracy the world's yearly production of zinc. The bulk of the metal will, however, have been produced direct from ore, possibly about 75 per cent., leaving 25 per cent. for remelted metal recovered from scrap metal, galvanisers, ashes, &c. The world's output of spelter from the early days of the industry to modern times has been given previously. The quantities of spelter produced by the chief countries for the ten years ending 1913 are shown in the following table.

<sup>1</sup> J. Gilbert, Mining Journal, London, 1916, vol. cxiv, p. 487.

1.5

Countries	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.	1912,	1913.
			Spelte	Spelter (in metric tons, 1000 kilos. = 2204·6 lb.). <sup>1</sup>	ric tons, 1	tooo kilos	. = 2204	6 Ib.). <sup>1</sup>		1
Germany	191,060 139,982	197,184 145,592	205,023 152,461	208,707 154,492	216,876 165,019	220,080 167,100	227,747 172,578	250,393 195,092	271,064 200.198	283,113 197.703
Holland Great Britain	13,099 46,216	13,767 50,927	14,650 52,587	14,990 55,595	17,257 54,473	19,548 59,350	20,975 63,078	22,733 66,956	23,932 57,231	24,323 59,146
riance and Span	49,082 9,248 10,606	50,309 9,357 7,642	53,780 10,780 9,610	55,733 11,359 9,738	55,819 12,761 8,839	56,118 12,638 	59,141 13,305 8,631	64,221 16,876 9,936 6,680	72,161 19,604 8,763 8,128	71,023 21,707 7,610 9,287
Production in Europe United States of America Australia	459,293 165,850 290	474,800 183,245 650	498,897 202,092 1,026	510,614 226,838 996	531,044 189,941 1,087	542,779 240,446	565,455 250,627 508	632,887 267,472 1,727	661,081 314,512 2,296	673,912 320,283 3,724
Total about	t 625,400	658,700	702,000	738,400	722,100	783,200	816,600	902,100	006'116	006'266
Yearly average price Average monthly price	£ 5. d. 22 11 10	£ s. d. 25 7 7	£ s. d. 27 I 5	£ s. d. 23 16 9	£ s. d. 20 3 6	<i>£ s. d.</i> 22 3 0 23 3 4 21 6 3	<i>k s</i> . <i>d</i> . 23 0 0 24 1 9 22 1 1	<i>k</i> s. d. 25 3 2 27 12 6 22 19 2	£ s. d. 26 3 4 27 5 10 25 8 10	<i>£</i> 5. <i>d</i> . 22 14 3 25 19 1 25 19 1 20 11 2

Production of Zinc. Compiled by Henry R. Merton & Co., Ltd. (London). <sup>1</sup> To convert to English long tons, multiply by 0.9842.

THE ZINC INDUSTRY

#### THE MARKETING OF ZINC

From the figures on p. 158 it will be seen that the absolute and relative contributions of Europe and the United States to the world's production of spelter for the years 1910-1913 are as follows:—

		Eur	ope.	United	States.
	Year.	Metric tons.	Per cent. of world's output.	Metric tons.	Per cent. of world's output.
1910		 565,500	69.3	250,600	30.7
1911 1912	•••	 632,900 661,100	70•2 67•6	267,500 314,500	29·7 32·2
1913		 673,900	67.5	320,300	32.1

Consumption.—One of the difficulties in estimating the amount of zinc used in the Arts is that variable proportions of old material are used with new material, and in consequence the consumption sometimes exceeds the total production for the year. The estimates of consumption take no account of any stocks which may exist, and hence, theoretically, the total consumption should yield the same figures as the total production.

Taking into account stocks at German works, the actual consumption of spelter in Germany during 1911 was about 217,900 tons, in 1912 about 220,800 tons, and in 1913 about 221,800 tons. When the stocks of other countries are taken into account, the returns show that prior to the war the production for the years named was in excess of the consumption.

The following table shows the absolute and relative contributions of Europe and the United States to the world's consumption of spelter for the years 1910–1913.

		Eur	op <b>e.</b>	United	States.
	Year.	Metric tons.	Per cent. of world's output.	Metric tons.	Per cent. of world's output.
1910 1911 1912 1913		 599,400 652,400 667,700 675,000	73:4 72:3 68:2 67:7	244,500 251,600 312,900 313,300	29•9 27•8 31•9 31•4

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$

# CHAPTER X

#### THE INDUSTRIAL APPLICATIONS OF ZINC

THE most important use of metallic zinc is in galvanising, which probably consumes more than 70 per cent. of the total output. The manufacture of brass probably utilises another 20 per cent., while the remaining 10 per cent. is used for conversion into sheets and for minor purposes, such as the production of alloys other than brass.

Galvanising.—The process of zincing, or, as it is termed, galvanising, which was discovered by Crawford in 1837, consists in depositing a very thin coat of zinc on iron, whereby the latter is preserved from oxidation by the atmosphere. In the United Kingdom galvanising has become an important branch of metallurgical industry and is very extensively practised, the chief centres of production being the Birmingham, Wolverhampton and South Wales districts.

Galvanising may be effected by the method known as hot galvanising (immersion in molten zinc), by the electrolytic process, by Sherardising, or by Schoop's metal-spraying process.

The hot galvanising process was, however, responsible for the production of practically all the 850,000 tons of galvanised sheets and wire exported from the United Kingdom in 1913.

In this process the iron is first freed from scale by immersing ("pickling") in hydrochloric acid, then washing well and scouring with sand. After cleaning, the plates or other articles are immersed in the galvanising bath, which is contained in a wrought iron pot, and consists of molten zinc covered with a layer of ammonium chloride.

The strength of acid used for pickling varies with the nature of the work. In the United Kingdom a 20 per cent. solution of hydrochloric acid is generally used for iron sheets, and acid of 12 per cent. strength for iron wire and tubes. The pickle is used cold, or nearly cold, and the operation is complete in a few minutes. At some works, particularly on the Continent, dilute sulphuric acid is used in place of hydrochloric acid for reasons of economy, but in this case a longer immersion is necessary. The temperature of the galvanising bath determines the thickness of the zinc coating ; the hotter the bath the thinner the deposit. The solvent action of zinc on iron, according to Diegel,<sup>1</sup> increases gradually up to about 490° C., above which temperature it rises very rapidly, being thirty times greater at  $530^{\circ}$  C. than below  $490^{\circ}$  C.

The iron sheets may be passed, after their passage through the bath, between rolls or wire brushes to remove superfluous zinc, and thus reduce the consumption of zinc. This treatment considerably improves the surface of the sheets. Zinc of good quality should be used for the galvanising bath. as the presence of lead exceeding 2 or 2.5 per cent. renders the zinc unsuitable for galvanising, the lead being easily dissolved by most soft waters, thus exposing the surface of the galvanised metal and hastening corrosion. Galvanised sheets often exhibit a beautiful moiré-metallique surface, due to the crystallisation of the zinc. When it is especially desired that the finished articles shall have a spangled appearance, from z to 3 per cent. of tin is sometimes added to the zinc bath. The addition of aluminium is said to increase the fluidity of the galvanising bath, owing to its deoxidising action, and also to its influence in effecting the separation and precipitation of the iron that accumulates in the bath. The aluminium should be added in the form of a zinc-aluminium alloy with a melting point below 480° C. Corrugated iron sheets form a considerable portion of the galvanising trade; these are often galvanised plain and then passed through the corrugating machine. The galvanising of iron wire, such as is employed for fencing, signal wires, &c., is performed with great rapidity, the coiled wire being annealed at the same operation. For this purpose the coiled wire is drawn through a furnace of such length that the wire in its passage through it is heated to redness, whilst the heated wire, as it passes out from the furnace, is directed by guide pulleys through a reservoir of dilute sulphuric acid (pickle), which has

<sup>1</sup> Journal of the Society of Chemical Industry, 1915, vol. xxxiv, p. 1147.

the effect of cleaning off any scale. On leaving the pickle it passes through a quantity of sand, whereby the wire acquires a clean metallic surface before it enters the bath of molten zinc. In this manner, whilst one end of the wire is still passing through the annealing furnace, the other extremity is being wound on to a drum in its galvanised state.

Owing to the great ease with which zinc is attacked by acids, galvanised iron is not adapted as a constructive material where it would be exposed to acid vapours.

In addition to sheets and wire, the process of galvanising is applied to chains, links, and many other articles requiring to be protected from corrosion.

The hot galvanising process yields two by-products : (1) hard zinc and (2) flux skimmings. The former is an alloy of zinc and iron, containing from 2 to 5 per cent. of iron, resulting from the gradual contamination of the zinc bath with iron. Being heavier than zinc, this alloy sinks to the bottom of the bath in pasty masses, and is removed from time to time by means of a perforated iron ladle, and cast into plates, which, when broken, exhibit a close-grained fracture with black spots characteristic of zinc containing iron. Part of this alloy passes into commerce for use where a zinc-iron alloy is required, and the remainder is liquated to separate as much zinc as possible. For this purpose the alloy is usually remelted at a high temperature, when it separates into two layers, the top layer consisting of tolerably pure zinc, which is carefully ladled off. The bottom layer is much less fusible, and forms a hard crystalline or granular material of the colour of zinc, but less lustrous. This ferriferous zinc is very friable, and frequently exhibits surface colorations of great beauty; it contains about 7.5 to 9 per cent. of iron, and is sold to the zinc smelters, who recover the zinc by a special redistillation.

The scum that accumulates on the surface of the galvanising bath and known as "flux skimmings" is removed from time to time. It consists of chloride and oxide of zinc together with some ammonium chloride and dirt. It is sold to the smelters, who treat it, usually by distillation, for the recovery of the zinc.

The disposal of the waste pickling liquors, which contain about 15 per cent. of hydrochloric acid and 10 per cent. of iron, chiefly as ferrous chloride, has caused considerable trouble in many localities where galvanising is carried on, and special

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processes have been devised to deal with them. Hitherto the usual system has been to neutralise the acid with lime and subsequently to roast the precipitate of ferrous hydroxide so obtained in order to convert it into red oxide of iron, which is sold.

The great increase in the price of zinc since the outbreak of war seriously affected the galvanising industry and led to the adoption of other methods and of substitutes, such as electro-galvanising, which consume much less zinc, and galvanising with lead, either by the hot process or by electro-deposition. Although it is not easy to disturb the settled demand for a world-wide commodity such as galvanised sheets, there are obvious possibilities in substitutes, once the buyer is familiarised with them and finds them cheaper. Experience. shows that substitutes for zinc will probably hold some of the ground they have temporarily acquired.

The electro-galvanising process has gained considerable favour in recent years, and its use is rapidly extending for certain classes of work, as it possesses several important advantages over hot galvanising. These may be summarised as follows: (1) greater economy in the use of zinc, as a much thinner deposit than that afforded by hot galvanising is sufficient to prevent rusting; (2) more complete control of the thickness of the coating on various surfaces; and (3) suitability for articles, such as steel springs, which have been subjected to special heat treatment and must not be heated to the temperature of molten zinc. Another advantage claimed for electrolytic galvanising is that it reveals defects, such as fine cracks, &c., in the iron, which would be concealed by hot galvanising. On the other hand, the electro-galvanised surface is dull or "dead" and not so pleasing in appearance as that produced by the older method. Although a large number of solutions have been tried for

electro-zincing, the general opinion amongst practical operators is that solutions of the sulphate, either alone or with other salts, give for general purposes the most trustworthy results, with the minimum of trouble in working.<sup>1</sup> In practice, the zinc is usually employed either in the form of a neutral solution of the sulphate or dissolved in excess of caustic soda.

" Sherardising."-In the process of coating iron and steel with zinc, introduced by Sherard Cowper Cowles, and known as <sup>1</sup> "Electro-Plating," Barclay and Hainsworth, London, 1912, p. 312.

"Sherardising," the articles, after being thoroughly cleaned by pickling, &c., are heated in metal drums, or boxes, in contact with zinc dust at a temperature of from  $260^{\circ}$  C. to  $425^{\circ}$  C. Vaporisation of the zinc dust takes place, the metal vapour then condensing on the surface of the iron articles. A zinc dust having a high metallic content will give the best coating. The condensed zinc slowly combines with the iron, giving a coherent protective coating that is highly resistant to corrosion.

The iron content of the Sherardised coating is a function of the temperature. The process is therefore carried out at the lowest temperature that is economically possible to secure a low iron content in the coating, since a high iron content is detrimental to the weathering properties of the coating.

The Sherardised surface is light grey in colour, with a dull or matte finish, but it is capable of receiving a high polish and made to resemble nickel plate. The process is economical and yields a superior product, and will doubtless receive more attention in the future than has been hitherto accorded to it. It is specially adapted for coating articles having a pattern or design on the surface which would become filled up and obliterated if the ordinary galvanising process were employed. Iron screws which have been galvanised by Sherardising are ready for use without further treatment. Narrow tubes can be galvanised inside by Sherardising, and this process has been used for coating with zinc the iron 5 pfennig pieces recently introduced in the coinage system of Germany.

The process of galvanising, patented by Schoop, of Zurich, consists in projecting a spray of pulverised zinc on to the goods, previously cleaned and warmed, until a zinc deposit about  $o \cdot r$  mm. thick is produced. The adherence of the deposit is said to be perfect. In the latest development of the spray process the zinc in the form of strip or wire is fed at a uniform rate into an oxy-hydrogen or other flame (or even an electric arc) sufficient to melt it readily. As fast as the metal melts a stream of compressed gas directed on it carries it away in a state of fine subdivision on to the surface to be coated. In practice, a specially constructed "metal spray pistol" is used for producing the spray. Very promising results are said to have been obtained by this process in Belgium and France, where it is in use on a large scale.

#### THE ZINC INDUSTRY

## Rolled or Sheet Zinc

Zinc lends itself well to rolling into sheets when the operation is carried out at a temperature between 100° C. and 150° C., within which range the metal is most malleable and ductile. In spelter intended for rolling, a small percentage of lead is desirable, as it improves the rolling qualities of the zinc, but the amount should not exceed I per cent. The rolled zinc of commerce is therefore a nearly saturated solution of lead in zinc. since it usually contains I per cent. of lead. Iron increases the hardness and impairs the malleability of zinc and should not exceed 0.15 per cent. In practice, it is usual partially to refine the spelter by liquation, so as to reduce the lead and iron to the minimum practicable by such methods, and when the refining has been properly conducted these amounts have little or no effect upon the malleability and ductility of the zinc. The metal to be used for rolling into sheets is cast in open moulds into flat ingots or plates which, whilst still hot and at the proper temperature, are rapidly passed through the rolls until the correct gauge is attained. For convenience, the ingot moulds are sometimes arranged in a circle on a rotating table.

Most of the zinc rolling is done on the Continent in Silesia and Belgium. The output of sheet zinc in Belgium in 1913 was 51,500 metric tons. A small quantity is rolled in the United Kingdom, chiefly at Birmingham, where zinc was first rolled early in the last century. There are also zinc rolling mills in the United States.

Prior to the war it was usual to import Continental zinc for rolling in this country, as it contained more lead than most of the British brands, which after refining are relatively free from lead, and are mainly employed for the production of alloys. It is customary when rolling Continental zinc to remove the excess of lead by liquation, as previously stated. In addition to the small amount of zinc rolled in this country, more than 20,000 long tons of foreign sheet zinc are annually imported into the United Kingdom. It would thus appear that there is ample scope for the extension of the British zinc rolling industry. A very large proportion of the zinc sheeting annually produced is employed for roofing purposes, mainly on the Continent. The metal is used either in the original sheets, or in the form of ornamental stamped tiles, which are nailed to the roof in an inclined position in the same way as slates. As a roofing material, sheet zinc is durable, light and efficient. Although up to the present it has found little application in the United Kingdom for roofing, its uses for this purpose have become so extensive in Continental countries that the spelter market is very materially influenced by the prosperity or otherwise of the general building trade.<sup>1</sup>

Thin sheet zinc finds application for a variety of purposes. In this form it lends itself readily to stamping in dies, and stamped ornaments in zinc were first produced in 1852. Within recent years it has found very considerable use for ceilings, the metal being stamped with varied ornamental designs in relief. It finds employment in the manufacture of many articles in ordinary domestic use, such as bath-tubs, pails, toys, &c. Metal of thinner gauge is used for the lining of air-tight wooden cases, hermetically sealed by soldering, for export to tropical countries. When perforated, sheet zinc is used for screens, sieves and other purposes. Rolled zinc plates of specially high quality find important use in the photographic reproduction process known as photo-zincography and in photo-etching.

Hot zinc sheets with a fine smooth polished surface are employed for producing the satinised surface finish on the better-class papers.

Thick rolled zinc plates, sawn to suitable sizes and drilled for bolting, are used to a considerable extent in marine boiler work to prevent corrosion of the boiler plates. For this purpose the zinc is bolted into position in different parts of the boiler, and owing to its being highly electro-positive it is first attacked by the corrosive influences and can be renewed when necessary. It is essential, however, that thorough metallic contact between the surfaces should be made to obtain full advantage of the protective influence of the zinc.

## Zinc Castings

The use of zinc in the foundry is somewhat limited, the demand for the cast metal being very small. It contracts but slightly on solidification, and is thus well adapted for castings. The castings made at a high temperature are brittle and largely

<sup>&</sup>lt;sup>1</sup> J. C. Moulden, *loc. cit.*, p. 522.

crystalline; but when cast near the solidifying point they are more malleable. Overheating of the metal, with its attendant losses, should be carefully avoided. Ammonium chloride (sal ammoniac) is recommended as the best flux, its action being to convert the floating dross from a pasty mass to a "dry dust."

Aluminium is recommended as the best deoxidiser, to be added after skimming, in the proportion of 0.001 per cent., and in the form of thin sheet clippings; the fluidity of the molten zinc is thus increased.<sup>1</sup>

Owing to the facility with which lead segregates, especially if the metal is poured at a high temperature, no brand of zinc containing more than 0.5 per cent. of lead should be used in the foundry.

Dies or blocks upon which hats are shaped are made of cast zinc. Cast zinc dies are used in the dental laboratory for swaging artificial metal-dentures. It is also employed for monuments, statues and tombstones, under the name of white bronze.

Spelter is also largely used for the production of "slush" castings for ornamental purposes.

In these, the metal in the mould is poured back into the ladle as soon as a thin layer has solidified on the face of the mould. These hollow castings must be sound, not merely for strength, but because they are all ornamental in character, and are usually required to be subsequently plated. The moulds are usually made of bronze, and many of the shapes are such as to cause excessive strains in the solidified zinc. The castings are polished and plated or otherwise finished. Makers of intricate slush zinc castings find it necessary to use metal of high grade, otherwise the castings are very liable to crack. Indeed so much is this liability to crack an indication of the quality of the metal that a number of the makers of highgrade zinc in America use the slush mould as a means of testing their product.

Cast zinc rods find extensive application in battery cells for electrical work. Rods are also prepared for this purpose by rolling, or by extruding the metal. Zinc of high grade should be used in their manufacture, as the life of such rods is much longer than of rods made from ordinary brands of spelter.

The employment of zinc for the manufacture of seamless pipes

<sup>1</sup> The Foundry, 1915, vol. xliii, p. 233.

for water supply has been advocated in recent years.<sup>1</sup> The pipes are made from pure "hard" zinc and have a diameter up to 80 millimetres. They can be tin-lined if required. Two pipes can be joined in the usual manner by widening the end of one and inserting the end of the other, or by covering the adjacent ends with a sleeve, and soldering. Tin solder is used, preferably with a stearine flux. The manufacture of the pipes is simple, and their bending easy. The pipes are as useful for water supply as lead pipes, and have the advantage of being much safer from a hygienic point of view, as no injury has been found to arise from the traces of zinc which are dissolved by water. Zinc is cheaper than lead for this purpose, and on account of its lightness the pipes do not require such strong wall supports. A pressure of 500 atmospheres is required to burst the pipes. These pipes cannot, however, be used for a hot water supply on account of the great expansion of zinc. In some recent tests by Rinck<sup>2</sup> tap water of medium hardness was sealed up in large zinc pipes with air excluded. After a year the amount of dissolved zinc was 2 to 3 milligrammes per litre. Physiological tests over a long period with water containing 7 to 8 milligrammes of zinc per litre gave no indications of injurious results.

## Other Uses of Zinc

Metallic zinc plays an important part in several metallurgical operations, notably in the precipitation of gold and silver in the cyanide process, the desilverisation of argentiferous lead by the Parkes process, and the reduction of silver chloride in gold refining.

Large quantities of zinc are used annually in South Africa and elsewhere for precipitating gold from cyanide solutions by means of zinc shavings. The precipitation is usually effected in wooden or steel troughs (known as zinc boxes) containing shavings of zinc coated with precipitated lead, formed by dipping the shavings into a strong solution of lead acetate. The zinc shavings are very thin and light, and are carried on iron gratings

<sup>&</sup>lt;sup>1</sup> Wittus, Jour. Gasbeleucht. 1913, vol. lvi, pp. 936–937. Abstract, Journal of the Society of Chemical Industry, 1913, vol. xxxii, p. 957.

<sup>&</sup>lt;sup>2</sup> A. Rinck, Zeit. Untersuch. Nahr. Genussm., 1914, vol. xxviii, pp. 99–103. Abstract, Journal of the Society of Chemical Industry, 1914, vol. xxxiii, p. 883.

through which the auriferous solution passes. The gold is precipitated on the zinc as a black mud, and is recovered by dissolving out the excess of zinc with acid. After drying, the gold mud is melted with fluxes and the resulting metal refined. From 5 oz. to r6 oz. of zinc shavings are generally needed for each ounce of gold recovered. The consumption of zinc in South Africa, chiefly for this purpose, amounted to 4,867 tons in 1914.

The employment of zinc in the desilverisation of lead is based on the fact that when molten zinc is stirred with a bath of argentiferous lead, which is afterwards allowed to cool, a crust forms on the surface consisting of zinc alloyed with silver and any gold and copper that may be present.

In the Parkes process, the solid zinc in slabs is thrown on the surface of the molten lead, and when it is melted the mixture is well stirred and then allowed to cool. The total amount of zinc added varies according to the content of silver, but is usually from  $1\frac{1}{2}$  to 2 per cent. of the weight of the argentiferous lead, and it is added in two or three lots, as several treatments with zinc are necessary to remove all the silver. The zinc crusts that form on the surface are removed by means of perforated ladles, the crusts being kept separate.

Fresh additions of zinc are made until the lead contains only about one-sixth of an ounce (0.0005 per cent.) of silver per ton. The zinc crusts, which are largely contaminated with lead, are submitted to liquation, whereby the lead separates and flows away, leaving the enriched scum behind.

The rich scums are distilled so that a large proportion of the zinc is recovered and is available for further use. The residue consists chiefly of lead, and contains from 5 to 10 per cent. of silver, which is recovered by cupellation. It is essential that fairly high-grade zinc be used for the Parkes process, as certain impurities, particularly iron, cause a much larger consumption of zinc. The process is carried out in large cast iron pots holding as much as 50 tons.

Zinc plates are used to a limited extent for the reduction of silver chloride resulting from the refining of gold. For this purpose the silver chloride is melted and cast into slabs, which are encased in flannel bags and boiled in water to remove base metals. The slabs are then arranged alternately with zinc plates in a tank of acidulated water, whereby the silver is reduced by electrolytic action. In modern practice, however, iron plates have been substituted for those of zinc.

Attention has already been directed to the use of zinc balls for the precipitation of impurities in solutions that are to be submitted to electrolysis. Recently the use of zinc balls for the precipitation of gold in cyanide solutions in place of zinc shavings has been suggested and introduced at several mines.

Metallic zinc has also been used for coinage. A new coin consisting of pure zinc, and representing in value the  $\frac{1}{800}$ th part of a piastre, was legalised in 1905 for circulation in Indo-China.<sup>1</sup> In that year 60,000,000 pieces, valued at £21,600, were struck at the Paris Mint.

#### Zinc Dust (Blue Powder)

There is a limited market for zinc dust, which, as previously pointed out, is a by-product from the distillation process. When zinc vapour is cooled too rapidly after distillation, or if it becomes too largely diluted with other gases, it condenses, not as fluid metal, but in the form of a fine bluish-coloured powder, consisting of an infinite number of minute globules coated with oxide, which prevent it from coalescing by ordinary means. Some of this substance, which is known as "Zinc Dust," "Blue Powder," or "Poussière," is always formed during the process of distillation, and is usually found in the "prolongs" beyond the condensers.

and is usually found in the "prolongs" beyond the condensers. The amount produced varies from 3 to 10 per cent. of the total zinc present when retort smelting is used, but with electrothermic processes the quantity is usually much larger.

The commercial value of zinc dust depends upon its content of metallic zinc, and the best grades contain from 86 to 92 per cent. of zinc in the metallic state.<sup>2</sup>

The commercial standard is that it shall pass a 100-mesh sieve and not contain more than 10 per cent. of zinc oxide.

Zinc dust is considerably more active chemically than spelter, being oxidised readily, and having the power to absorb hydrogen. On this account it finds many uses in chemical industries, being used to discharge locally the colour of dyed cotton goods and in the preparation of the indigo vat. It is used as a precipitant for

<sup>&</sup>lt;sup>1</sup> Thirty-sixth Mint Report, 1906, p. 31.

<sup>&</sup>lt;sup>2</sup> J. C. Moulden, loc. cit., p. 524.

the removal of copper, antimony, arsenic, &c., from electrolytic solutions containing these and other metals.

It has also been used for the recovery of gold and silver from cyanide solutions of these metals, for which purpose it has been stated to be more efficient than zinc shavings. Latterly it has found increasing favour for this purpose, as the small amount of lead it usually contains acts beneficially in promoting more rapid and complete precipitation of the gold and silver.

Reference has already been made to its use in the Sherardising process.

Care has to be exercised in the storage of zinc dust, owing to the readiness with which it will fire if exposed to moist air, or wetted, when in bulk. Serious fires and even explosions have been caused in this manner.

## CHAPTER XI

#### INDUSTRIAL ZINC ALLOYS

ZINC enters into the composition of a number of important alloys, to which, when present in certain proportions, it communicates hardness without impairing the malleability of the alloy. In larger proportions it often renders the alloy brittle.

Owing to the comparatively low melting point and volatility of zinc, the preparation of its alloys requires considerable care to prevent unnecessary loss of the metal.

Modern research has shown that the mechanical properties of metals and alloys are materially influenced by the presence of small quantities of impurities, and has emphasised the necessity of employing pure metals in the preparation of alloys. This has led, in the case of zinc alloys, to an increasing demand for zinc containing less lead and other impurities than are usually present in commercial spelter.

The economy and other advantages resulting from the use of high-grade zinc for alloying purposes are so great that brass and other alloy makers who have once employed it will never resort to ordinary spelter if they can help it. To meet this demand various works in the United Kingdom are producing a considerable amount of high-grade metal by distillation, and also by electrolytic processes.

There are but few alloys in which zinc is the main constituent, the chief being the so-called anti-friction metals, but in smaller proportion zinc is a valuable constituent in several very useful alloys.

The alloys of industrial importance in which zinc is a constituent are (1) those consisting of zinc and copper, constituting the numerous varieties of brass; (2) those consisting of copper, zinc, nickel, forming the so-called "German or Nickel Silvers"; and (3) zinc with tin and other metals known as "anti-friction metals."

Brass.-Brass was first made by the Romans shortly before the Christian era, and was used both for coins and ornaments. The ancient name of the alloy was latten, which is still retained in the French word laiton. In the Middle Ages the Germans were famous for the production of brass, which was imported into this country, principally from Cologne, chiefly in the form of rectangular pieces known as Cullen plates; this was employed for the so-called " brasses " of churches, particularly in the Eastern Counties. More than 4,000 such brasses are known to exist in various churches. &c., in the United Kingdom, which is far richer in this respect than any other country. The first works for the production of brass in England are stated to have been erected by a German, at Esher in Surrey, about the middle of the seventeenth century, copper being imported from Sweden for its manufacture. Its manufacture was started in Bristol in 1702, and brass works were erected in Birmingham about 1740 by the Turner family. Birmingham is now the principal seat of the brass industry of this country, and so rapid has been the development within recent years, that in Birmingham alone prior to the war more than 35,000 persons (male and female) were employed in the brass trade, the value of the metal consumed amounting to four millions sterling.

Considerable impetus was given to the brass industry in the early part of the eighteenth century by the introduction of rolling mills, with the subsequent application of powerful stamping machinery, in 1769, which enabled articles to be produced in sheet metal more rapidly, with better finish and with less metal than by the process of casting hitherto exclusively employed.

Among the more important factors that have contributed to the enormous development of the zinc industry in more modern times must be mentioned the introduction of gas fittings, in the early part of the nineteenth century; the use of brass tubes in locomotives and marine engines; the introduction of yellow metal sheathing; the extended uses of brass for engineer's work, and for water fittings, &c.; and more recently the very extensive employment of the metal for electrical fittings. Until the middle of last century, brass was exclusively made by the old process of "cementation," in which metallic copper was heated in crucibles in contact with calamine (zinc ore) and carbon, whereby zinc was liberated and combined with the copper to form the alloy known as "calamine brass." This ancient process was superseded by the direct preparation of brass which is now exclusively employed. This is effected by melting together a mixture of copper and zinc, either in crucibles, or when very heavy castings are required in a reverberatory furnace.

When prepared in crucibles the zinc is added to the copper immediately after the latter is completely melted, the ingots of copper having been heated to redness prior to their introduction into the pots. In making castings, and in the remelting of brass, there is always a considerable loss of zinc through volatilisation, for which allowance must be made when arranging the mixture.

The clay or graphite crucibles usually hold about 90 lb. of metal, but much larger pots are sometimes employed. The crucibles are heated in small wind furnaces burning coke as fuel, or in furnaces heated by gas or oil.

Zinc and copper alloy in all proportions, the resulting products being of uniform composition throughout, as the metals do not segregate. The colour and properties of the alloys vary with the relative proportions of the metals. When the alloys are of a decidedly yellow colour they are known industrially by the general term "brass," although many special names have been introduced by different makers to represent one and the same alloy, thus giving rise to considerable confusion.

The term white brass is given to alloys in which zinc predominates, giving a white alloy. As a result of the work carried out by modern methods of research, our knowledge of the constitution of alloys of the zinc-copper series has advanced considerably of late years. The constitution of alloys rich in zinc is very complex, but these alloys are of little industrial value; on the other hand, the constitution of the alloys rich in copper which constitute the brasses proper is comparatively simple. With a few exceptions the zinc-copper alloys of industrial importance may be said to contain from 50 to 70 per cent. of copper, and within this range there are three constituents or phases, which are respectively designated by the Greek letters a,  $\beta$ , and  $\gamma$ .

Research has shown that in certain mixtures of metals there is obtained one or more classes of crystal formation, depending on the mutual solubility of the two metals. Thus iron and nickel dissolve in one another in all proportions and give only one type of crystals, no matter what the proportions. On the other hand, zinc and copper are not mutually soluble in all proportions. Starting with pure copper and adding zinc, the limit of solubility is reached with 36 per cent. of the latter metal. Up to this point only a-crystals are observed under the microscope, beyond it  $\beta$ -crystals appear with the  $\alpha$ -crystals, and later y-crystals appear. The Alpha-constituent consists of a solid solution of zinc in copper, the maximum content of zinc being as stated, about 36 per cent. at 400° C. The Gamma-phase was regarded by Shepherd as a solid solution, but as the result of more recent research there is evidence to show that the Gamma-phase contains a definite compound, Cu<sub>2</sub>Zn<sub>3</sub>, containing about 40 per cent. of copper. The Beta-constituent contains about 52 per cent. of copper and has the pro-perties of a solid solution. According to Carpenter,<sup>1</sup> however, the so-called Beta-constituent splits up into an intimate mixture of Alpha and Gamma on cooling from a critical temperature of 470° C. On heating above this temperature the reverse change takes place. This critical temperature is found in all alloys containing from 60 per cent. of zinc down to 28 per cent., and probably less.

The Alpha-phase is relatively soft and ductile, and the Betaphase is harder and less ductile, while the Gamma-phase is still harder and very brittle, and can be readily powdered in a mortar. As the Gamma constituent is very brittle, the fact that the stable phase above  $470^{\circ}$  C. is Beta, and below this temperature Alpha *plus* Gamma, has an important bearing on the cause of the brittleness and decay of many brasses in engineering work (Carpenter)

The brasses containing more than 64 per cent. of copper consist of a single homogeneous solid solution, while those containing from 55 to 64 per cent. of copper are composed of two constituents, each of which is a solid solution. Rapid cooling from a suitably high temperature is capable of profoundly modifying the structure and constitution, and consequently the properties, of the zinc-copper alloys.

<sup>1</sup> Journal of the Institute of Metals, 1911, i, vol. v, p. 127.

The constitution of the chief commercial brasses has been classified by Hudson<sup>1</sup> as follows :---

Copper per cent.	Nature of Constituent.
100-71 71-64 64-63 63-53·5 53·1-51 51-40	Consists entirely of Alpha-phase at all temperatures. Alpha-phase below 400° C., Alpha <i>plus</i> Beta above. Alpha <i>plus</i> Beta at all temperatures. Alpha <i>plus</i> Beta at low temperatures, Beta only at some higher temperature. Consists entirely of Beta at all temperatures. Beta <i>plus</i> Gamma at low temperatures, Beta only at higher temperature.

It will be noted that the proportion of the Beta-constituent increases as the temperature rises, and this fact has important bearings on the heat treatment of brasses. As shown by Charpy, the effect of adding zinc to copper is to increase the tenacity and to diminish the ductility.

With more than 40 per cent. of zinc, however, the tenacity very rapidly decreases, whereas the ductility is diminished after the addition of 30 per cent. of zinc.

Consequently, for ductile brasses the limit of zinc is usually about 30 per cent., and in cases where a combination of ductility and strength is required, as with brass for cold-drawn tubes, or for cartridge cases, an alloy of about 70 per cent. of copper and 30 per cent. of zinc is preferred.

The industrial brasses may be conveniently considered under three heads, viz.: (I) Cast brass, (2) low brass (*i.e.*, low coppercontent) for hot rolling, and (3) high brass (*i.e.*, high coppercontent) for cold rolling.

(1) Cast brass is very variable in composition, but with the exception of a few alloys rich in copper used in the manufacture of cheap jewellery, &c., the usual composition of cast brass is about 66 per cent. of copper and 34 per cent. of zinc, which is known as English standard brass. It casts well, and is capable of being rolled and hammered and even drawn into wire if so required.

(2) Low brasses suitable for hot rolling contain from 55 to 63 per cent. of copper. The commonest of these yellow brasses is that known as Muntz metal, patented by G. F. Muntz in 1832,

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<sup>&</sup>lt;sup>1</sup> Journal of the Society of Chemical Industry, 1906, vol. xxv, p. 503.

and consisting of 60 per cent. of copper and 40 per cent. of zinc. Although Muntz metal was originally introduced for sheathing wooden ships, it is now chiefly used, either under the name of Muntz metal or "yellow brass," for the cheaper varieties of brass tube, wire and sheet.

Muntz metal is hardened by quenching, and the explanation of this is readily seen from its structure. With increasing temperature the Alpha-constituent is dissolved by the harder Beta-constituent until, at  $720^{\circ}$  C., the alloy containing 60 per cent. of copper consists entirely of the Beta-constituent. If, now, the alloy is quenched from this temperature the separation of the Alpha-constituent is hindered, and the alloy will be found to be stronger but less ductile than before.<sup>1</sup>

(3) *High brasses*, suitable for cold rolling, usually contain more than 60 per cent. of copper. Whereas these alloys are readily workable in the cold, they are quite brittle when hot, and, therefore, cannot be subjected to hot working. The best alloy of this class is the brass used for tubes and wire drawing, which contains 70 per cent. of copper and 30 per cent. of zinc. This alloy possesses the maximum elongation of the copper-zinc series combined with a considerable degree of strength. On this account it is used for the production of cartridge cases, alike for rifle, machine-gun and the lighter types of artillery, and is frequently referred to as "Cartridge" brass.

As it is subject to the severest of treatment, cartridge brass requires that both the copper and zinc shall be as pure as possible, 99.8 per cent. of zinc being a minimum, with 0.1 per cent. of lead and 0.1 per cent. of iron as maxima.

The annealing of brass is carried out in reverberatory furnaces, the temperature employed varying with the composition of the brass. In the case of cartridge brass, the maximum effect of annealing is reached at  $600^{\circ}$  C., whilst there is a very marked softening of the alloy at  $420^{\circ}$  C.

Industrial brass is capable of withstanding very drastic treatment, and in addition to rolling, drawing, stamping and spinning, it is capable of being extruded or forced through dies at temperatures somewhat below the melting point of the alloy. Great advances have been made within the last few years in the extrusion of brass, and complicated sections which it would be impossible to produce by rolling are now regularly manufactured by

<sup>1</sup> "Alloys," E. F. Law, London, 2nd edition, 1914, p. 179.

this process (Law). The alloys used for this purpose usually contain about 40 per cent. of zinc.

Brasses containing Iron.—The addition of iron to brass, first suggested by Kier in 1779, imparts special hardness, toughness, tenacity and wearing properties, whilst the alloy can be rolled either hot or cold. In more modern times brasses containing iron as an essential constituent have been introduced under special names, such as "Sterro-metal," or "Gedge's alloy," "Aich's metal" and "Delta metal," which may be taken as representative of the class.

These alloys, which are now largely used, consist essentially of yellow brass, containing from 55 to 60 per cent. of copper and 38 to 41 per cent. of zinc, with the addition of iron, which varies from 1.5 to 4.5 per cent. In addition to iron, small quantities of other metals are frequently added.

Sterro-metal contains 60 per cent. of copper, 38 per cent. of zinc, and 1.5 to 2 per cent. of iron, and Aich's metal is practically the same, although various analyses show that the percentage of iron present varies within somewhat wide limits, and tin is sometimes present. Sterro-metal can be made very hard and dense by suitable mechanical treatment, which has as great an influence in modifying its properties as its chemical composition. In rolling or hammering this alloy when hot, special care is requisite in regulating the temperature to which it is raised, as it becomes brittle when overheated, and cracks under the hammer or between the rolls.

Delta metal, introduced by Alexander Dick in 1883, varies in composition, an average composition consisting of approximately copper 55 per cent., zinc 42 per cent., with I to 2 per cent. of iron. In some cases small amounts of manganese, aluminium, tin or lead are added to the alloy to impart special properties to it.

Delta metal is stronger, harder and tougher than brass. It is easily cast, forged or stamped, and is capable of being rolled hot and drawn cold. In addition, it has a much greater power of resisting corrosion than ordinary brass, which enables it to be used for many purposes where such brass is inadmissible, more especially for shipbuilding, marine engineering and sanitary work. The maximum stress of Delta metal varies from 27.8 to 35.4 tons per square inch, according to the treatment to which it has been subjected. The constitution of the iron brasses does not a ppear to have been sufficiently investigated; when present in small amounts the iron appears to enter into the alloy as a solid solution and does not form definite chemical compounds (Law). When more than about 2 per cent. of iron is present, the iron and zinc would seem to combine. Formerly the iron was added to these alloys in the form of a copper-iron alloy, but this was not found to be entirely satisfactory, the metals in all probability not being properly alloyed. Dick, when he patented Delta metal, suggested the introduction of the iron in the form of an alloy of iron and zinc, which can be obtained of reliable composition, and is also relatively cheap as a by-product from the galvanising process. Since that time iron-zinc alloys have been largely used. The preparation of iron-zinc alloys for this purpose is dealt with subsequently.

Brasses containing Lead.—A small addition of lead is beneficial in brasses intended for turning, the best alloy, and that which is most commonly used, containing about 60 per cent. of copper, 38 per cent. of zinc, and 2 per cent. of lead; it is sometimes termed "clock brass." The lead is usually added after the zinc, and while the crucible is still in the fire, the temperature being kept as low as possible. Lead does not alloy with brass, but separates out in the form of globules and films between the crystals of the brass, a condition which necessarily weakens the metal, so that the addition of lead is only permissible where strength is of secondary importance. The fracture of brass containing lead is distinctly grey in colour, owing to the fact that the line of fracture passes through the lead.

The beneficial effect of lead in brasses intended for turning was known long before the nature of its influence was understood. Ordinary brass is difficult to turn owing to the character of the turnings, which are long and tenacious, and tend to foul the tools; a slow speed has also to be employed. On the other hand, the presence of lead in a free state in the brass renders the alloy less tenacious, and the turnings break off through the lines of weakness caused by the lead, so that chips are produced instead of spiral turnings. The lead also appears to act as a lubricant, with the result that a much higher speed can be employed and a better finish given to the work. Brass containing not more than 2 per cent. of lead can be rolled, but the alloy is rolled cold, on account of its liability to crack if rolled hot.

Brass containing Tin.-A small percentage of tin renders brass,

and more especially low brasses of the Muntz metal type, less liable to corrosion by sea-water when in contact with gun-metal. On this account brasses containing tin are employed in naval construction, the alloys being known as "naval" brasses. They contain approximately 62 per cent. of copper, 37 per cent. of zinc and I per cent. of tin. The mechanical properties of brass are not seriously affected by the addition of I per cent. of tin, but beyond this amount there is a rapid increase in brittleness and hardness, whilst with more than 2 per cent. the alloys lose their useful properties.

Many of the more important of the copper-zinc alloys are those containing about 60 per cent. or less of copper in which part of the zinc is replaced by small quantities of one or more other metals, such as those mentioned above. The number of such special brasses is now increased by the so-called vanadium bronzes, in which cupro-vanadium is used as one of the ingredients. The actual effect of vanadium in alloys does not appear to be very great.

Alloys of Zinc and Iron.—With iron zinc forms a series of alloys which are generally white, hard and brittle. When the iron does not exceed about 5 per cent. the alloys are less crystalline and darker in colour than pure zinc; such alloys are produced in the process of galvanising, and are known as "hard zinc." The alloys become greyer, harder and more brittle as the iron content is increased. The alloy obtained by saturating zinc near to its temperature of volatilisation with iron is not attracted by a magnet; it does not rust, nor give sparks by friction or blows. It is dense in structure, but is only semi-metallic in fracture, and contains about 22 per cent. of iron.

The zinc-iron alloys have a somewhat important application in the preparation of the special yellow brasses, such as Delta metal, which contain from 1.5 to 4.5 per cent. of iron, and to which reference has been previously made.

The necessary zinc-iron alloy is prepared commercially either (I) by direct union of the constituent metals, or (2) by the treatment of hard zinc from galvanising. The alloys actually used in practice generally contain from 7 to nearly 30 per cent. of metallic iron.

The production of the zinc-iron alloys by direct fusion of the metals is difficult owing to the high melting point of iron and the volatile character of zinc. When prepared by this method, clean iron wire, or sheet, is added to a bath of molten zinc heated to near its boiling point. The union of the metals is facilitated by the addition of a little charcoal and some solid ammonium chloride. This method of preparation is usually accompanied by a considerable loss of zinc.

Alloys rich in iron are usually obtained commercially by liquating the hard zinc from galvanising works to remove part of the zinc, and then strongly heating the residue, which is rich in iron, in a closed crucible.

The excess of zinc is thus volatilised, leaving a zinc-iron alloy in which the content of iron increases with an increase in the temperature employed.

Nickel Silver or German Silver.—The white alloys manufactured under these names consist essentially of nickel, copper and zinc. An alloy composed of these three metals was known in early times in China, and was exported to Europe in the eighteenth century under the name of "pack-fong," or white copper. Pack-fong seems to have been recognised as a triple alloy of nickel-copper-zinc in 1776, when Engeström published what appears to have been the first analysis. The manufacture of a white alloy composed of these metals was first started on a commercial scale at Berlin, about the year 1824, and was subsequently exported to the United Kingdom as a cheap substitute for silver, and it is probably owing to this fact that the alloy became known as "German silver."

Although alloys of nickel-copper-zinc are now usually known in the trade under the general term of nickel silver, they probably exist under a greater number of special names than any other alloy, since different manufacturers employ fanciful names to denote alloys containing different proportions of the constituent metals which they consider best suited to produce an alloy of good white colour and possessing satisfactory working qualities. Thus Nevada silver, Virginia silver, Potosi silver, Silveroid, Arguzoid, &c., may be given as examples.

The term nickel silver is somewhat misleading, as the alloy does not contain silver. If a nomenclature which indicates the true nature of the alloy be adopted, it would be described as a zinc-cupro nickel, but it is probably more convenient to call it a nickel brass, and this term is now usually adopted by research workers on these alloys, although this name has to a certain extent unfortunately become associated with the alloys of the coppernickel series containing no zinc and used for coinage purposes.

The nickel silver alloys are now prepared largely as a basis metal for electro-plating upon, and as a substitute for silver for the manufacture of table forks, spoons, &c., the chief centres of production being Sheffield and Birmingham.

In the form of wire they are used for electrical resistances. The percentage of zinc in the industrial alloys varies from 20 to 35 per cent., and it is added as a substitute for the more expensive metal nickel.

The various grades of nickel silver in general use in the United Kingdom are known in trade circles as firsts, seconds, thirds and fifths, which contain approximately the following percentages of nickel: firsts, 20 per cent.; seconds, 16 per cent.; thirds, 12 per cent.; fifths, 7 per cent.; the content of copper appears to vary between 56 and 59 per cent.

The alloy known as seconds is used by many firms as the basis metal for electro-plate wares of best "A I" quality, although an alloy of higher nickel content is preferred by others. The seconds alloy is also largely used for the manufacture of best quality nickel silver spoons, forks, &c., that are sold as such and not plated.

The character of the silver deposit in relation to the composition of the basis metal has been studied by McWilliam and Barclay,<sup>1</sup> who conclude that when the proportion of nickel exceeds 14 per cent. the silver is more liable to strip off irregularly in actual use. It seems advisable, therefore, to avoid too high a percentage of nickel in the basis metal for high-grade electroplate which has to endure rough usage. Although the alloys poor in nickel are not so white and not so strong as the richer alloys, the importance of the colour is not so great where there is a heavy deposit of silver.

Owing to the high temperature required for the fusion of the nickel, and the low melting point and ready oxidisability of zinc, the preparation of nickel silvers is attended with a loss of zinc, and special care is accordingly required in their production. To overcome this difficulty the alloys are made by melting together an alloy of copper and nickel (usually containing 50 per cent. of each metal) and brass. The copper-nickel alloy has a lower melting point than pure nickel, whilst the brass has a higher

<sup>1</sup> Journal of the Institute of Metals, 1911, vol. v, p. 214.

melting point than zinc, and the melting points being thus more nearly alike, the metals are more readily alloyed and the loss of zinc by volatilisation is very materially reduced. This method answers the double purpose of lessening the oxidation of the zinc and of more readily producing a homogeneous alloy. The alloys are made by melting the metals in the usual way in graphite crucibles. Shortly before pouring the metal a small quantity of manganese is usually added to ensure thorough deoxidation of the alloy. The metal is cast in iron moulds similar to those used in brass casting, but of different sizes.

In constitution the nickel-silver alloys, when cast, exhibit the characteristic structure of quickly-cooled solid solutions, but, on annealing, the crystallites undergo gradual absorption and are replaced by the regular crystalline structure of simple metals and homogeneous solid solutions, the addition of zinc to the copper-nickel alloys not being attended with the formation of compounds. They may be regarded either as brasses containing nickel in solution, or as copper-nickel alloys containing zinc in solution. The nickel silvers are greyer in colour and harder than silver, and are capable of receiving a high polish; their fracture after casting is strongly crystalline, and the alloys require, in the first instance, careful annealing before rolling or hammering; but after the crystalline character has been thus overcome, the metal may be hammered, rolled or stamped into a variety of forms, whilst some specimens possess considerable elasticity. The alloys of nickel, zinc and copper become brittle when hot and are therefore always rolled and drawn in the cold. Most of the alloys acquire a vellow tarnish when exposed to the atmosphere, and in acid solutions, such as vinegar, with access of air, they become coated with a layer of verdigris, the rate of corrosion varying with the nickel content of the allov.

As in the case of most solid solutions, the alloys are softened by annealing. This is effected in reverberatory furnaces so constructed that a reducing atmosphere is, as far as possible, maintained and oxidation kept at the minimum.

The temperature of annealing, which is of great importance, has been found by recent research to vary from 700° C. to 900° C., according to the composition of the alloy, the higher temperature being employed for the alloys of high zinc content. In works practice annealing from twenty minutes to an hour, according to the thickness of the sheets, at a temperature of about

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750° C. is sufficient to render the metal soft enough for all purposes.

For ornamental castings, nickel silver containing I or 2 per cent. of tin is frequently used; the presence of tin, however, even in small quantity, makes the alloy decidedly yellow in colour; it also renders it brittle and unfit for rolling.

It has been frequently asserted that the brass and nickel silver made in Germany and America, and imported into the United Kingdom prior to the war, is superior in working qualities to that produced in this country. Whilst there is undoubtedly some truth in this assertion, it is well to bear in mind that this superiority of product has only been attained by the use of pure metals, and the application of scientific knowledge to the melting, casting and heat treatment of the alloys, and also to scrupulous cleanliness in all the processes through which the metal passes during manufacture. All these conditions for the production of high-grade metal are equally available to British manufacturers, and it is gratifying to know that within recent years many firms have availed themselves of the rapid advancement of scientific knowledge in the preparation and treatment of metals and allovs, and are now producing metal equal in quality to any supplied from foreign sources. On the other hand, it is unfortunately true that there is still a considerable number of manufacturers who appear to have inherited a certain conservatism, and a tendency to cling to "rule of thumb" methods which may produce alloys suitable for certain classes of work, but they frequently fail to produce the high quality metal required to withstand the severe mechanical treatment to which brass and other non-ferrous alloys are now subjected in modern manufacturing processes, as in the production of cartridge cases.

Anti-friction Metals.—Zinc enters into the composition of a number of so-called anti-friction alloys, or white metals, used for bearings. Bearing linings of white metal are indispensable for certain purposes, as they are soft and enable the axle to adapt itself to the condition of the bearing and run with much less friction than in the case of harder alloys. This tendency of white metal to reduce friction has given rise to the term "anti-friction " metal, which is now generally used for such alloys. One great advantage of white metal alloys for this purpose is their low melting point, which permits of a worn-out bearing being readily melted out and replaced by a new one. The white metal is generally melted in an ordinary ladle, and when the journal or mandril is wiped dry and chalked, the molten metal is poured in.

Since the introduction of white-metal bearings an immense number of so-called anti-friction metals have been placed upon the market. The composition of these varies very considerably, and they may contain copper, tin, zinc, antimony and lead; but seldom more than three of these metals are used in any one alloy.

Whilst zinc in small proportions enters into the composition of many anti-friction metals, the alloys in which the percentage of zinc preponderates form a comparatively small class.

The composition of a number of white metals in which zinc is the chief constituent is given in the table on p. 190.

From these figures it will be seen that the zinc content may reach 90 per cent. The alloys of zinc, tin and antimony possess a high compressive strength, and they are employed for bearings of machinery, such as rock-breakers, where strength is of more importance than perfect anti-frictional qualities.

Zinc Alloys for Die-casting.-Within recent years white metal alloys containing zinc have found extensive application in the production of die-casting or casting under pressure in steel moulds. In this process the molten metal is forced into the die or mould under a pressure of 100 to 400 lb. per square inch, the pressure being transmitted by a mechanically or hand-operated plunger, actuated by compressed air or by centrifugal force. The alloys used for the production of die-castings are generally white metals of low melting points. The shrinkage of the alloys is an important consideration, and involves special provision in making the moulds. The shrinkage of zinc-base alloys, that is, those in which zinc is the main constituent, is said to be about twice as great as that of tin-base and lead-base alloys and about one-third that of aluminium-base alloys. In a zinc-base alloy the shrinkage is given as 0.004 inch per inch of dimension, thus indicating the care required in making the dies, which are made of special alloy machinery steel. The cost of the dies is very considerable, but upwards of 100,000 duplicate castings, each accurate, may be made from a properly constructed die, thus making the die-cost per casting small.

In ordinary practice, die castings are made to dimensions of plus or minus 0.001 inch to each inch of dimension.

The temperature of the dies and of the metal varies with the

## INDUSTRIAL ZINC ALLOYS

different alloys used, so as to assist in controlling shrinkage. The zinc-base alloys may contain zinc 50-80, tin 5-30, copper 2-20, aluminium 2-6, and antimony I-5 per cent. A considerable range of alloys is thus available in this series. The following alloys may be given as representative of zinc-base white metal for die-casting.<sup>1</sup> Nos. I and 2 are stated to be suitable for ordinary work in place of brass, No. 3 is harder and No. 4 harder still.

			No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.	No. 4. Per cent.
Tin	  n	       	73·75 14·75 5·25 6·25 —	72·7 19·0 5·0 1·0 2·0 0·3	73.8 12.0 10.6 3.4 	46·2 30·8 20·4 2·6 —

ZINC-BASE DIE-CASTING ALL
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Gas furnaces may be used for melting the metal, the pot being covered to prevent oxidation, and the metal forced through a tube and nozzle into the moulds.

The advantages of die-casting are low cost of production and interchangeability, together with greater degree of accuracy in the case of small castings—than is possible by machinery. The introduction of die-castings has done much to facilitate the work of the foundry, as the process is adopted for making intricate parts which would be expensive to cast in sand, to stamp in dies, or to machine. The accuracy of die-castings having holes, screw threads, teeth, &c., is as great as with ordinary machined parts. Owing to technical difficulties the limit in weight of average diecastings is given as 5 lb., although in special cases the weight may be as high as II lb. Some of the uses of die-castings are as bearing magneto parts, electric lighting and starting systems, speedometer housings, &c., in automobile work, and as parts in automatic machines, cash registers, &c.

Alloys of Aluminium and Zinc.—The importance of alloys of aluminium and zinc has long been recognised, but it is only within recent years that the price of aluminium has enabled its alloys to be used on a large scale. Zinc forms solid solutions with aluminium, and the alloys of these metals, either alone or more

<sup>1</sup> Engineering, 1914, vol. xcvii, pp. 144-145.

often with small additions of other metals such as copper or magnesium, are practically the only aluminium alloys of industrial importance.

The alloys are largely used in connection with munitions of war, as in certain parts of shells, in aeroplane construction, in the motor industry and for many other purposes where strength and lightness are desired.

Only the aluminium-zinc alloys containing less than 40 per cent. of zinc are single homogeneous solid solutions, and they are therefore the only ones of practical value. Those containing up to 15 per cent. of zinc are soft enough to be rolled or drawn, whereas beyond this amount the alloys are hard and more suitable for castings, as they are easily worked. In practice the alloys usually contain from 10 to 20 per cent. of zinc, with the addition of a small quantity of copper. The properties of the aluminiumzinc alloys have been investigated by Rosenhain and Archbutt,<sup>1</sup> whose mechanical tests indicate that alloys containing from 15 to 25 per cent. of zinc (with or without addition of copper) would be more serviceable than alloys containing less than 15 per cent. of zinc, which are much more widely used in present practice. If dynamic as well as tensile tests be taken into consideration, the alloy containing 20 per cent. of zinc appears to be the most useful of the binary alloys. A characteristic feature of the alloys is the very large effect produced upon them by hot work. When the alloys are heated, the tensile strength falls rapidly,

When the alloys are heated, the tensile strength falls rapidly, but the hot alloys exhibit a considerable amount of ductility, so that it is possible to roll into bars alloys which are brittle in the cast state. The alloys containing respectively 25 and 20 per cent. of zinc attain their maximum tensile strength when in the form of rolled bar  $1\frac{1}{4}$  in. diam., the figures for the two alloys being : ultimate stress, 27.5 and 22.64 tons per square inch ; yield point, 25 and 17.3 tons per square inch ; elongation on 2 in., 16.5 and 20.5 per cent. respectively. The alloys, with and without addition of copper, differ from most non-ferrous alloys in that in the rolled condition they exhibit a definite and well-marked yield point. All the alloys containing from 10 to 30 per cent. of zinc are very easily machined. Corrosion tests in sea-water showed that the loss of weight increases with increasing zinc content. The rapid corrosion (especially in moist air) frequently observed with commercial aluminium-zinc alloys is attributed <sup>1</sup> Tenth Report to the Alloys Research Committee, Inst. Mech. Eng., 1912. to the presence of impurities derived from the spelter employed in their production.

The alloys are now very generally melted by means of coalgas as a fuel. Melting is performed either in graphite crucibles or very commonly in cast iron pots, which are preferably protected by a wash of inert material.

Miscellaneous Zinc Alloys.—The Biddery ware manufactured at Bidar in India usually contains about 90 per cent. of zinc together with copper, lead, and tin in different proportions. Two analyses of Biddery metal are given in the table on p. 190.

Zinc alloys readily with silver, the alloys rich in silver presenting some resemblances to the corresponding silver-copper alloys, although somewhat whiter in colour. They are malleable and ductile and take a high polish.

Silver-zinc alloys have long been used by native silversmiths in India for the production of silver wares. For this purpose the silver is usually alloyed with about 10 per cent. of zinc.

Zinc in small proportions also enters into the composition of a number of important industrial alloys.

The addition of a small quantity of zinc to certain alloys increases their wearing power, and for this reason it is added to the bronze used for coinage, which contains I per cent. of zinc, 4 per cent. of tin and 95 per cent. of copper. This alloy was first used in England in 1861.

A standard Admiralty bronze consists of 88 per cent. of copper, 10 per cent. of tin and 2 per cent. of zinc, whilst in some alloys of this class the percentage of zinc reaches 10 or even 15 per cent. Statuary bronze usually contains from 2 to 10 per cent. of zinc. The alloys used for this purpose lie midway between the bronzes and the brasses and usually contain a considerable percentage of lead.

The addition of zinc renders the alloy more fluid and greatly facilitates the operation of casting. Too much zinc, however, has to be avoided or the metal will have a brassy colour, and will not assume a pleasing "patina" on exposure to the atmosphere.

The class of alloys known under the name of Britannia metal, consisting of tin and antimony together with small quantities of other metals, not infrequently contains zinc.

The percentage of zinc is, however, usually under 5 per cent., as it increases the hardness and brittleness of the alloy, and is therefore not a desirable constituent if present in large amounts.

### THE ZINC INDUSTRY

The composition of typical industrial alloys in which zinc is an important constituent is shown in the accompanying table.

	 	 	 	 <b>r</b>	

0			Comp	ositic	on per	cent.			
Alloy.	Zinc.	Copper.	Tin.	Lead.	Nickel.	Antimony.	Iron.	Aluminium.	Remarks.
Anti-friction Metals- Anti-friction metal . Babbits' metal (so	85°0	5°0				10,0			
called) Bearing metal	60°0 8°0	4°0 82°0	19 <sup>°</sup> 0 10°0	5'0 	···· ···	3°0 		 	For locomotive axles.
", bard . Bearing metal medium hard	2°0 6'0	82°0 67°5	16°0 21°5	•••	····			···	
Bearing metal Lumen bearing metal	20°0 85°0	76'0 10'0	3.0	1'0 		 		5°0 6'0	Daimler motor-bus bearings.
Special ", ", Vaucher's alloy . Brasses—	82°0 75°0	12'C 	18.0	4'5		2°5			For journal lining.
Aluminium brass Best yellow brass .	38'o 30'o	60°0 70°0				•••	···· ···	2*0 	Sheet, wire, tubes, cartridges, &c.
Brass	5°0 29°0	94°5 70°0	 1'0	 		 	o*5 		High-pressure turbine blades. Condenser tubes. Admiralty specification.
,, to be machined Cast brass (so called),	38.0			2.0					specification
very variable Naval brass Ordinary brass	43°0 37°0 33°3	57°0 62°0 66°6	1.0	 	···· ····				Admiralty specification. Wires, sheets, &c.
Aich's metal Delta metal (average	38.0	60'0	•••				2'0		
composition) Munt2 metal Parson's white "brass"	36°0 40°0 30°0	60'0	2'0  65'0	1'0 			1.0		Sheathing.
Sterro metal Brazing solder Bronzes—	55`5 50'0	42°0 50°0		•••			2.5		
Coinage bronze (British)	1'0	95'0	4'0						A due too lare N.
Gun metal .	2°0 1'0	88°0 86°0	13,0 13,0						Admiralty No. 1. Admiralty No. 2A to resist high pressure.
Manganese bronze . Parson's white bronze White bronze "German Silvers" (so called)—	42°0 38°5 29°0	54°5 2°5 4°5	1'5 56'5 65'0	 0'5 	···· ···	1'5 1'5	1.0 1.0	0'5 0'5 	0'5 Mn (composition varies).
Firsts . Seconds	28'0 24'0	56°0 62°0			16°0				
Thirds Fourths Fifths	32 <b>•</b> 35 • 36 •	55'0		•••	12'0 10'0	···· ···		···· ···	
Miscellaneous- Admiralty metal	28.5	1'5	 70°0		7°0 				For work under water.
Ashberry metal . Biddery ware .	1'0 84'3	2'0 11'4	80°0 1°4	2'9	···· ···	14°0 	 		Other metals 3 per cent. Manufactured in India.
Motor alloy	93'4 10'0	3'5 2'0		3.1				88.0	Light alloy for motor-car work.
White button metal .	80°0	20'0	•••						

Typical Zinc Alloys.<sup>1</sup>

<sup>1</sup> Compiled from tables in Law's Alloys, and other sources.

## CHAPTER XII

### COMMERCIAL COMPOUNDS OF ZINC : ZINC PIGMENTS

OF the various compounds of zinc of commercial value zinc oxide is by far the most important. It is largely used as a pigment under the name of zinc white, and is valued for its permanency, as it is not blackened by sulphuretted hydrogen like white lead, for which it is a substitute. Although it lacks the body and opacity of white lead, it has good covering power, and is nonpoisonous.

The zinc oxide of commerce is prepared either (I) direct from zinc ore or (2) by the combustion of crude spelter. One of the best known direct methods is the Wetherill process, which is largely used in the United States, especially in New Jersey and Pennsylvania. The ore treated is obtained from the mines of Franklin Furnace, New Jersey, where it is crushed and concentrated, first by magnetic separators and then by jigs, giving four products.<sup>1</sup>

The first, franklinite, consists mainly of oxides of zinc, iron and manganese, with practically no injurious impurities.

This ore is worked by itself, making the best qualities of oxide. The manganiferous residue remaining in the furnace after removal of the zinc is treated in blast furnaces for the manufacture of spiegeleisen. The second product contains about the same amount of zinc as franklinite, but less iron and manganese, and does not make quite so good an oxide. It is used, like franklinite, for the manufacture of oxide, and the residues are thrown away.

The third product is willemite, anhydrous zinc silicate, which is used for the production of high-grade zinc. The fourth

<sup>1</sup> Plant of the New Jersey Zinc Company. Oil, Paint, and Drug Report, Nov. 2nd, 1914.

product consists of limestone tailings. The ore is shipped to Palmerton, where a very extensive plant produces enormous quantities of zinc oxide annually. The plant comprises 54 blocks of furnaces with a total grate surface of about one-half acre. Each furnace, known as a "Wetherill grate," consists of a brick chamber with an arched roof and a flat grate, under which is a closed ashpit. The ore is mixed with the quantity of powdered anthracite necessary for its reduction, and then spread over a layer of burning anthracite on the perforated grate of the furnace, through which a low blast from a fan is forced, producing an underdraught. The zinc is volatilised and burned to oxide by the excess of air above the charge. The zinc oxide so produced and the products of combustion are drawn from the furnace by large exhaust fans which draw them over to the bag-rooms. These are provided, at the top, with distributing pipes, from which hang muslin bags about 45 feet long and 6 feet in circumference. The combustion gases pass out through the bags and the oxide is collected in them. The bags are connected with hoppers at the bottom, from which the finished oxide is drawn to be taken to the packing room. The six bagrooms contain nearly 71 miles of bags, with a total surface of 511 acres of muslin. The oxide is first sifted through wire screens, and then fed into a packer which forces the oxide into barrels or bags. The barrels are made at the works and contain 300 lb. of oxide each. For smaller quantities paper bags, containing 50 lb. each, are used.

The Wetherill process is also carried out at Liége and other places, but the ore used is generally zinc blende, which is first converted to oxide by roasting.

Leclair's process of making zinc oxide by distilling and burning metallic zinc, started between 1840 and 1850, is still in use in Europe and also at the Florence works of the New Jersey Zinc Company of Pennsylvania.

In the Silesian method, the spelter is heated to its boiling point in retorts, and the vaporised metal is conveyed into chambers through which air is kept in circulation, when the metal burns, and the oxide, with more cr less metallic zinc, is deposited in a series of condensing chambers. As the crude spelter always contains some lead, which in this process would be converted to oxide and impart a yellowish tint to the zinc white, impairing its commercial value, a small quantity

## COMMERCIAL COMPOUNDS OF ZINC : ZINC PIGMENTS

of gas containing carbon dioxide is introduced into the retort. By this means the lead is converted into carbonate, which is considerably heavier than the zinc white, and therefore settles first in the condensers.

In Belgium, zinc white is also made by burning spelter in the manner described, but the final product is purified by levigation. The spelter used in Belgium contains up to 2 per cent. of lead, but the purified product contains under 0.2 per cent. of lead, with very small amounts of iron, and zinc oxide from 99.69 to 99.99 per cent.

Commercial zinc oxide nearly always contains lead compounds (carbonate or basic sulphate), the presence of which affects its market value. It has been claimed that zinc white made direct from the ore is a more durable pigment than that obtained by burning spelter.

Zinc oxide is prepared for pharmaceutical purposes by precipitating a solution of zinc sulphate with sodium carbonate and igniting the basic carbonate thus thrown down. Zinc oxide is a pure white, amorphous powder, which when heated becomes yellow, but again becomes white on cooling. When ignited at a high temperature it shrinks and becomes hard and gritty. It is infusible at all ordinary temperatures, but distinctly volatile at a white heat. The oxide does not fuse in the oxy-hydrogen flame, but, like lime, in these circumstances becomes intensely incandescent; for some time after being so heated it appears phosphorescent in the dark.

The oxide prepared by burning the metal has a specific gravity of 5.6. It is insoluble in water, and does not combine directly with water to form the hydroxide. It dissolves in acids, producing the different zinc salts.

Commercial zinc oxide is not infrequently adulterated with barium sulphate (barytes), which is cheap and blends well with the oxide.

An impure zinc oxide, known as zinc grey, is obtained as a by-product in the manufacture of zinc white. It is used as a silver-grey paint, and, when made into a paste with wood oil, as a cement for steam joints.

Lithopone.—The important zinc pigment known as lithopone, or Orr's zinc white, was first produced by T. B. Orr in 1874 (English patent of Feb. 10). Theoretically it is a mixture in molecular proportions of zinc sulphide and barium sulphate, but

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the products on the market contain other substances as well.<sup>1</sup> The advantages claimed for it are that it is not affected by sulphides and has high covering power, and its disadvantages, due to particular methods of manufacture, are that on exposure to sunlight it often turns grey and becomes chalky. It is prepared by mixing solutions containing equivalent quantities of barium sulphide and zinc sulphate. As in the case of other white pigments, purity of raw materials is essential, iron compounds being very objectionable.

Barium sulphide is obtained by roasting ground barytes (barium sulphate) with coal or other carbonaceous material in a reducing atmosphere, either in a flat bedded reverberatory furnace or in a rotary kiln of the Brückner type. Lixiviation of the product of the roasting gives a solution of sufficient purity for the purpose.

For the zinc sulphate solution any zinc-bearing material may be used. Spelter and dross, when treated with sulphuric acid. leave little or no zinc in the insoluble residue, but zinc ashes usually leave so much mud in the solution tanks that the unit of zinc in this material is not so valuable. Iron and manganese when present are usually removed by boiling with bleaching powder. The two solutions in proportionate quantities are then mixed to produce the mixed precipitate, which is filter-pressed and dried. In some cases about 0.5 to 1.0 per cent. of a mixture of freshly prepared magnesia and common salt is added to the precipitate before filtration. The dried precipitate is mixed with 3 per cent. of ammonium chloride, and the whole heated to dull redness to give it body, which it lacks if not sufficiently heated. Excessive heating converts some of the zinc sulphide into oxide. Some oxide is always found in lithopone, but it should not exceed 2 per cent.; it ranges, however, in commercial samples from 0.5 per cent. to as much as 12 per cent. After burning, the red-hot pigment is at once quenched and ground fine, after which it is thoroughly washed, dried, disintegrated, usually in pebble mills, and then packed.

Ordinary lithopone contains about 29.5 per cent. of zinc sulphide. A higher grade, containing from 45 per cent. to 48 per cent. of sulphide, is produced by replacing part of the barium sulphide by sodium sulphide, and washing out the resulting ' "Lithopone," H. S. Riederer, *Journal of the Society of Chemical* 

Industry, 1909, vol. xxviii, p. 403.

sodium sulphate: Lower grades are also made by replacing part of the zinc sulphate by sodium sulphate. When used for outside painting, lithopone is frequently mixed with other pigments, so as to prevent the darkening which takes place when it is exposed to sunlight. Unlike ordinary zinc white, lithopone is free from lead.

Lithopone is chiefly made in the United States, and the quantity made has increased considerably within recent years. The amount produced in the United States in 1912 was 24,220 short tons; in 1913 the output was 29,685 short tons.

Zinc-lead pigment, or leady zinc oxide, consists of a mixture of zinc oxide and sulphate, lead oxide and sulphate, with some sulphurous acid and water. Commercial samples contain lead up to about 25 per cent. The output of this pigment has been rapidly increasing. It is usually produced by the treatment of zinc-lead concentrates, or residues containing these metals.

Zinc oxide also finds limited application in the glass industry for the production of opal glass, and also in the preparation of crystalline glazes for pottery and stoneware, as such glazes are less liable to "craze" than lead glazes.

Zinc chloride, ZnCl<sub>2</sub>, is formed by the direct combination of zinc with chlorine, or by the action of hydrochloric acid upon the metal. The latter method is adopted for the production of zinc chloride on a large scale. For this purpose scrap zinc is placed in hydrochloric acid contained in a stone, cast iron or wooden vessel. The solution so obtained is neutralised with sodium carbonate, warmed to 40° or 50° C. and bleaching powder added to precipitate iron and manganese. When the precipitate has settled, the clear solution of zinc chloride is siphoned off and boiled down in enamelled iron pots. The evaporation is continued until the temperature of the liquor is 230° or 240° C., a little potassium chlorate is added to oxidise any organic matter, and some pure hydrochloric acid carefully poured into the hot solution to dissolve any basic salt. The mass is then allowed to solidify, and while still warm is packed in iron drums of from 30 to 50 kilos. capacity, which are at once closed air-tight.

When the aqueous solution of zinc chloride is evaporated, partial decomposition takes place, hydrochloric acid being evolved and basic compounds precipitated, consisting of combinations of the chloride and oxide. Hence, during the concentration of the liquid in the preparation of zinc chloride, hydrochloric acid is added to re-dissolve this compound.

The anhydrous chloride is a greyish-white, soft, waxy-looking substance, which is readily fusible, melting at 262° C. to a clear, mobile, highly refractive liquid; at a higher temperature it volatilises and distils without decomposition, with the produc-tion of peculiarly irritating fumes. It deliquesces rapidly on exposure to moist air, and is very soluble in water or alcohol, its solution being powerfully caustic.

From a strong aqueous solution, deliquescent crystals are deposited on evaporation, having the composition  $ZnCl_2, H_2O$ . A concentrated solution attacks and dissolves vegetable fibre,

consequently it cannot be filtered through paper; it should be filtered through asbestos or glass wool. When a solution of zinc chloride is electrolysed, chlorine is evolved and crystalline zinc deposited.

Zinc chloride is extensively used as a preservative of timber, and it acts as a powerful dehydrant. It is much used for railway sleepers, either alone or in combination with creosote. American railroad companies buy sleepers specified to contain  $\frac{1}{2}$  lb. of zinc chloride per cubic foot, equal to about 0.5 per cent. of zinc. The textile industry absorbs considerable amounts, and it is used in "mercerising" or giving the appearance of silk to cotton goods. In dilute aqueous solution it is employed as an antiseptic,

acting as a powerful disinfectant and germicide.

Zinc chloride for medical purposes is usually cast in the form of small rods or tablets. A paste made by moistening zinc or small rods or tablets. A paste made by moistening zinc oxide with zinc chloride rapidly sets to a hard mass; this mixture, under the name of oxychloride of zinc, is employed in dentistry as a filling or stopping for teeth. Many of the oxychloride cements used for this purpose contain small amounts of other ingredients, such as powdered glass or silica, to confer greater hardness on the mass when set. Other zinc compounds used as cements by dentists are oxy-phosphate and oxy-sulphate. The former consists of zinc oxide mixed with one of the forms of phosphoric acid; and the latter is a mixture of zinc oxide and calcined zinc sulphate made into a paste with a solution of gum arabic. Compared with metal fillings these cements usually lack hardness, but they are non-irritating and set fairly rapidly. They are all more or less readily acted upon by the fluids of the mouth. Zinc oxychlorides are also used as pigments.

Zinc Sulphate, or White Vitriol, known also as zinc vitriol, is prepared on the large scale either by the action of sulphuric acid on zinc or by the treatment of zinc sulphide ore (blende). In the former case commercial zinc scrap or zinc waste is dissolved in sulphuric acid, and the solution evaporated to the crystallising point. When produced from ores containing blende, these are carefully roasted to produce zinc sulphate, which is extracted with water, and the salt crystallised from its aqueous solution by evaporation. It was obtained, on a manufacturing scale, by this method as far back as the sixteenth century. The water from zinc mines is frequently charged with zinc sulphate which is extracted by crystallisation.

The salt crystallises with seven molecules of water in colourless rhombic prisms, which on heating fuse readily in their water of crystallisation. Commercial zinc vitriol is made to assume the shape of a sugar-loaf by stirring the fused salt in wooden troughs with wooden shovels until crystallisation takes place, and subsequently pressing the mass into moulds.

In common with all the soluble salts of zinc, zinc sulphate has an astringent taste, and is poisonous. It dissolves in less than its own weight of water at the ordinary temperature. When exposed to the air, the crystals slowly effloresce; if heated to roo<sup>o</sup> C. they lose six molecules of water, leaving the monohydrated salt,  $ZnSO_4$ , $H_2O$ . At a temperature of about 300<sup>o</sup> C. this is converted into the anhydrous compound, and at a white heat it gives off sulphur dioxide and oxygen, leaving the oxide.

Zinc sulphate is used as a mordant in calico printing, and is employed as a clarifying agent and preservative in the manufacture of glue. In medicine it is employed as an astringent, and a very weak solution forms a common eye lotion. It, however, finds its greatest application in the manufacture of lithopone, to which reference has already been made.

# CHAPTER XIII

#### THE FUTURE OF THE ZINC INDUSTRY IN GREAT BRITAIN

THE question of the future supply of zinc in sufficient quantity for the maintenance and development of the metal industries of this country, without the importation of foreign metal, has been brought into special prominence by the exceptional circumstances arising out of the world-war. The conditions which gave rise to the very serious position in which this country was placed at the outbreak of war in regard to her zinc supplies have already been referred to. It has been shown that during the past few decades the zinc market was becoming increasingly a German monopoly. The war has, however, fortunately brought about the beginning of a new epoch in the development of this important branch of non-ferrous metallurgy, and if certain comprehensive schemes, which have recently been formulated. for the treatment of Imperial zinc ores in the United Kingdom come to fruition, the increase in zinc production may be considerable.

The first essential in the development of any industry is a regular and ample supply of raw material, and where this is lacking progress is invariably retarded. Undoubtedly one of the obstacles to the expansion of the British zinc industry in the past lies in the fact that for many years the smelters have relied for raw materials chiefly upon the rich ores which have been shipped in comparatively small lots from foreign sources.

Before the war there was little difficulty in obtaining all the ore required to sustain the comparatively small output of metal hitherto produced in this country, the ore itself being moderate in price, whilst freights were low. Now the cost has greatly increased, and the expenses of ocean transport have advanced enormously and are likely to remain high for some time to come. In respect to ore supply the British zinc smelters have always been at a disadvantage compared with Continental and American smelters, both of whom have sufficient domestic supplies of ore available to augment that obtained from foreign sources, and to ensure a steady and plentiful supply of raw material. If Great Britain is going to produce all the zinc needed for home consumption, the pre-war output of metal will have to be increased at least five-fold, and this entails a corresponding increase in ore supply and the building of much new plant.

But, as already pointed out, the available supplies of the rich calamine ores, upon which British smelters have relied so much in the past, are steadily decreasing, and there is little doubt that in the near future the whole of the zinc of commerce will have to be smelted from zinc blende. In these circumstances it is very important that the supplies of this ore within the Empire should be utilised for the development of the Empire zinc industries, and not left to the exploitation of foreign concerns.

As it has not infrequently been asserted that the superior acumen and metallurgical knowledge of the Germans enabled them to obtain control of the Broken Hill concentrates and treat them successfully, it may be well to state, on the authority of Moulden,<sup>1</sup> that although the Germans obtained control of a large proportion of the huge output of Australian zinc concentrates, they did not treat them except in relatively small quantities. They utilised this control to make money, in which they were most successful, passing the major part of the concentrates on to the Belgian works for smelting. Of the total Australian output Belgium smelted at least 75 per cent. and Germany only 14 per cent. The Germans had placed themselves in a position to force this on the Belgian works by acquiring at the outset a controlling interest in a number of them.

In this connection it is well to remember that the export of Empire raw material to foreign countries for the recovery of the commercial products is most undesirable in the interests of this country. Not only is the benefit in wages, skilled employment and greater profits involved in the working up of the raw material to a refined metal lost to this country, but the art of producing the finished metal and its alloys, and the control of it, pass into alien hands. In this way supplies of indispensable metals, such as zinc, can only be obtained by paying

<sup>1</sup> Moulden, op. cit., p. 528.

enhanced prices, or may be cut off altogether in times of urgent need, as experience has unfortunately proved.

It may be well to repeat that the extensive deposits of zinc ore at Broken Hill. New South Wales, afford an ample supply of ore, sufficient to meet all the zinc requirements of the United Kingdom for some years to come, and now that the difficulties which at first attended the treatment of the ore have been successfully overcome, there is every reason why this ore should be smelted in preference to ores from foreign sources. The importance of treating Broken Hill zinc concentrates within the Empire, and more particularly in this country, becomes more apparent on reviewing the situation as created by the war. The effect of the outbreak of war on the zinc industry was felt more quickly in Australia than in Great Britain. The mines, deprived of the greater part of their market, had to curtail production very considerably, and it is to their credit that, in order to minimise hardships among their labouring population, they continued to produce considerably more ore than they could for the time being dispose of. Certain considerations bearing on the question of the future markets for Broken Hill concentrates have been enumerated as follows.<sup>1</sup>

(1) Australian legislation has been passed cancelling the contracts for the sale of Australian ores to alien firms and prohibiting them for the future, so that no zinc concentrates will be henceforth shipped to Germany. The Australian mine-owners will therefore have to find fresh markets for that considerable proportion of their ore which previously went to Germany or to the German smelters in Belgium.

(2) Germany, in spite of the length of time that her own ore deposits have been worked, has still large reserves. She has also considerable zinc-mining interests in China, and before the war shipped zinc concentrates from that country. She will not fail to develop her trade in this direction as far as she is able to do so after the war, and will continue to be an important producer of spelter.

(3) The United States zinc smelters will be formidable competitors after the war so long as high prices are maintained. They have used their large profits wisely in making their plants efficient and up to date, and in accumulating large financial reserves. Their present rate of production is sufficient for more than 70 per

<sup>1</sup> H. C. H. Carpenter, Nature, 1916, vol. xcviii, p. 129.

cent. of the world's peace requirements before the war. They will have considerable tonnages of the metal available for export. They have very large ore supplies, not only of "straight" zinc ores, but of the complex ores in which zinc blende is associated with galena and other metallic sulphides, and which now constitute an increasingly important source of spelter. It is very unlikely, therefore—quite apart from the ro per cent. *ad valorem* tariff to which zinc ores imported into the United States are liable—that Australian zinc concentrates will find a market in America.

(4) The Canadian Government is encouraging zinc extraction by granting bounties on zinc produced in Canada from Canadian ores. Australian concentrates are therefore not likely to enter Canada to any great extent.

(5) The future of the Belgian industry is quite uncertain, but it is much to be hoped that it will be re-established and the smelting works rebuilt after the war, and in this case, as it will depend largely on imported ores, there may be a renewal of the contracts with the Broken Hill mine-owners.

(6) By virtue of the magnitude of its population, its transport facilities, markets and the raw materials necessary for zinc smelting—apart from the ore itself—Great Britain is the most suitable country for the treatment of Broken Hill concentrates exported from Australia. The future development of the British zinc industry is largely dependent on the facilities that will be afforded for their treatment, by the adaptation and enlarging of existing works, and the erection of new works for the extraction of the zinc and other metals, &c., by distillation, or by electrolytic or other processes.

The Australian Government has dealt with the situation created there, and a scheme has been drawn up affecting the future of the zinc mining and smelting industry, and one in which Australia and Great Britain are immediately concerned. It does not appear probable that America will be able to compete in the supply of spelter at a reasonable price on the English market after the war.

A new company, known as the Zinc Producers' Association Proprietary, Limited, has recently been formed to handle all zinc concentrates produced within the Commonwealth. This is the largest and most powerful metal combination in the Southern Hemisphere, and one of the most important in the

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world.<sup>1</sup> The Commonwealth's annual output of zinc ores and concentrates amounts to 450,000 tons, and the gross value of metal is not less than  $\pounds$ 5,000,000. All the zinc-producing companies of Australia are members. The Association will act for all Australian producers of zinc ores who belong to it during the next fifty years, on a co-operative basis, the companies undertaking to have all their smelting done through it. One of the fundamental principles is "equality of treatment" of all members, irrespective of the tonnage of output. The Commonwealth Government is represented on the board, thus safeguarding the interests of the general community.

In spite of the Commonwealth Prime Minister's efforts in England, the spelter question has not yet been definitely settled so far as Great Britain is concerned. A contract has been entered into for a large supply of zinc concentrates per annum for Great Britain during the continuation of the war, with the option of increasing the quantity. The British Government has entered into a definite agreement for a term of ten years to take a minimum of 100,000 tons of Australian concentrates at satisfactory prices.

As to the remainder, arrangements have been suggested whereby Australia will treat locally 40 per cent. of the whole of the zinc concentrates produced in the Commonwealth.

The British Government has further contracted to take up to 45,000 tons per annum of spelter and electrolytic zinc produced in Australia for a period of ten years. The post-war requirements of France, Belgium and the other Allies are being considered.

In order to deal with some of the zinc concentrates reserved to Australia under the scheme, a company, called the Australian Electrolytic Zinc Company, has been formed, and will, it is hoped, be successful.

Contracts for power have been arranged with the Tasmanian Government; technical experts have been engaged in America, and the company promises to be one of the foremost industrial concerns in the Commonwealth. Towards securing capital for Australian zinc industries the Imperial Government undertakes to advance a substantial sum at the same rate of interest as is paid by the Imperial Government, if required, to finance Australian zinc works until war restrictions are removed. The

<sup>1</sup> Chamber of Commerce Journal, March, 1917.

Mount Lyell Company is embarking upon a new venture, and promises to be a large producer of electrolytic zinc. The enlargement of the Port Pirie zinc distillery is receiving attention. Zinc specialists have been engaged to undertake the modernisation of the zinc distilling plants in Australia, and also to install and work the electrolytic zinc processes. All the above provisions will, however, only permit of the treatment of a portion of the zinc concentrates which can be produced in Australia for which concentrating plant is already in existence. What is to become of the balance of the concentrates available for smelting is uncertain, but Japan has already made offers for purchasing considerable quantities.

With regard to the development of the British zinc industry there has been much discussion; it has been proposed to erect large smelting works in this country under Government subsidy, in addition to the extension of existing works, with a view to largely increase the output and render this country less dependent on foreign supplies. A special committee has been appointed by the Secretary of State for the Colonies and the President of the Board of Trade to elaborate a scheme. What is involved in this proposition is best seen by reference to the figures representing the output and consumption of zinc in the United Kingdom under normal conditions. From the few available statistics it would appear that the maximum production of spelter in this country in any year before the war was approximately 58,000 English tons, whereas the consumption was approximately 200,000 tons, the difference between production and consumption being 142,000 tons.

The actual production for 1913 was 58,298 tons, of which, as previously stated, probably not more than 31,290 tons was "primary" spelter, produced direct from ores, the balance of 27,008 tons being "secondary," or remelted metal from the treatment of by-products, &c. Thus secondary zinc forms an exceptionally abnormal proportion of the total British output.

Practically the whole of the primary spelter was produced from imported ores, the metal produced from British ores being comparatively insignificant and probably amounting to not more than 2,500 tons.

The consumption of virgin zinc in 1913 was 203,302 tons, of which no less than 145,004 tons was imported.

The actual consumption of spelter in 1913, after allowing for

imports of zinc wire and sheet, and that present in imported brass, was 224,000 tons, but even this does not include the zinc contained in zinc dust, zinc oxide, lithopone and salts of zinc (chloride and sulphate), figures for the import of which are difficult to obtain, but the quantities are by no means inconsiderable.

The imports of drawn and rolled zinc in 1913 were 18,768 tons. With regard to these imports it is of interest to note that in 1913 Germany imported 313,269 tons of zinc ore, 57,641 tons of spelter and 725 tons of drawn or rolled zinc, and exported in the same year 44,731 tons, 109,606 tons, and 24,965 tons of these materials respectively. It should be noted also that the British statistics refer only to the United Kingdom, and take no account of the imports of crude or manufactured zinc into Canada, Australia, South Africa and India, which were large.

From the above figures it will be evident that in order to render this country independent of foreign supplies of zinc it will be necessary to smelt sufficient ore to produce annually at least 140,000 tons more spelter than has been produced in the past.

Apart from the provisions that have been made recently for an adequate supply of zinc ore for British smelters there is very little information available as to what steps are being taken to increase the output of metal in this country. According to the latest report of the Inspector of Alkali Works, extensive additions were made to registered zinc works in 1916, but no new works were added. In 1916 the Sulphide Corporation acquired the smelting works of the Central Zinc Company at Seaton Carew, and in 1917 they purchased the sulphuric acid works constructed by that company for  $f_{52,000}$ . These works utilised the sulphurous gases coming from the zinc-roasting furnaces, The smelting works are to be doubled, and when this is accomplished they are expected to be able to treat 30,000 tons of Broken Hill concentrates yearly, equal to an annual output of zinc of about 12,000 tons. This tonnage amounts to one-half the Sulphide Corporation's output of zinc concentrates.

Considerable additions are also being made to the Swansea Vale Spelter Works, the largest works in the Swansea district. Good progress has been made with the extensions, which, when completed, will give an output of 15,000 to 20,000 tons of spelter per annum. Extensions are in progress, or completed, in other works, and according to a recent estimate when all the new plant is erected the total capacity of the British smelting works will be about 78,000 tons of primary spelter, made up as follows:<sup>1</sup>

Works					Capacity.
Swansea Vale	••	••		••	20,000 English tons.
English Crown	Spelte	r	• •		18,000 ,,
Vivians Seaton Carew	••	••	••	• •	10,000 ,,
	••	••		••	10,000 ,,
Dillwyn	••	••	••	••	8,000 ,,
Williams Foste					6,000 ,,
Sundry lesser ]	plants	••			6,000 ,,
	Total	••			78,000 English tons.

This estimate is based on the theoretical capacity of the respective plant extensions when finished; the actual production would naturally be lower. According to this estimate the total production of zinc from ores will be approximately 50,000 tons more than the pre-war output of virgin metal, or, including secondary zinc, an increase of nearly twice the pre-war annual output.

To encourage the smelting of Broken Hill concentrates by British smelters the Government, in connection with the British-Australian scheme, has guaranteed the minimum price of  $f_{23}$ for ordinary spelter and  $f_{28}$  for high-grade spelter.

An agreement has also been reached between the spelter producers in this country and the Ministry of Munitions on the subject of new works. The producing companies are to be allowed to deduct from their excess profits the difference between the cost of new production during the war and before the war; they are also to receive from the Ministry of Munitions a "reward" for extending their works, in that they will be allowed to deduct from their excess profits, before taxation, 50 per cent. of the pre-war cost of construction.

Before the war it was agreed by producers generally that it did not pay to produce permanently under  $f_{22}$  per ton. With existing methods and conditions of production, the cost for some time to come must be considerably more.

In these circumstances it is considered by many that the margin of profit is not sufficient to stimulate private enterprise. In this connection it may be permitted to quote the opinion of Mr. J. C. Moulden, who has had a wide experience in zinc smelting. Compared with the production of other metals in common use, he considers "that there is no branch of the metallurgical industry

<sup>1</sup> Mining Journal, London, 1917, vol. cxvi, p. 66.

in which, considering the difficulties and risks involved, the invested capital has been so ill-requited as that of zinc. What profits there have been were made largely by the ore what pronts there have been were made largely by the ore and metal-dealing firms, and those who, in addition to smelting, turned out rolled and stamped zinc together with lead and silver from complex ores—and possibly also zinc oxide." That zinc smelting can, however, be profitably undertaken, under favour-able conditions, and by the utilisation of all the valuable byproducts, with good management and if equipped with labour-saving appliances, is evident from the fact that the Continental zinc-smelting companies have in recent pre-war days paid dividends of 20 to 25 per cent. and over. Under the conditions that obtain in this country it seems obvious that the Government must undertake the cost of erecting new works if they want to see the position much further advanced, and it is the uncertainty of what they are going to do which makes an estimate of the outlook for home production so much a matter of hypothesis, and which prevents private capitalists from embarking. The problem is obviously a very different one for the Government in contrast to private enterprise. They have not merely to consider the question from the point of view of the price of spelter after the war. Beyond economic factors there is the consideration of the public safety in view of possible restrictions on the necessary supplies of sulphuric acid and spelter. Assuming that the above estimate of increased production is

Assuming that the above estimate of increased production is substantially correct, it will be evident that something like another roo,ooo tons of metal will be required to bring up the spelter production to correspond with the pre-war consumption, and it is to supply this extra output that the construction of smelting works by the Government has been suggested. The erection of smelting works at Avonmouth, capable of producing 24,000 tons of zinc per annum from Australian ore, has been proposed, and in this connection the Bristol City Council recently sanctioned the preparation of schemes for extending the accommodation of the Royal Edward Dock to meet the traffic incidental to the proposed shipment of zinc concentrates from Australia. Negotiations for the treatment of further quantities of these concentrates at Widnes, and possibly elsewhere, are also in progress. But after allowing for the carrying out of the present programme for the expansion of the productive capacity of existing works, even including the 24,000 tons per annum for the proposed new works at Avonmouth, it would appear that the possible output will be only about one-half the pre-war consumption. It is most unfortunate, in the future interests of the zinc industry in this country, and in the interests of the metal industries dependent on metallic zinc as raw material of first importance, that the Government has not, up to the present, taken any steps to begin the erection of new zinc-smelting plant. Moreover, it cannot be too strongly urged that the provision for increased zinc output so far suggested is inadequate to meet the situation, and the erection of large works would be one of the greatest factors in supplementing the zinc deficiency, and would help to keep the production in our own hands and remove our dependency on metal from foreign sources.

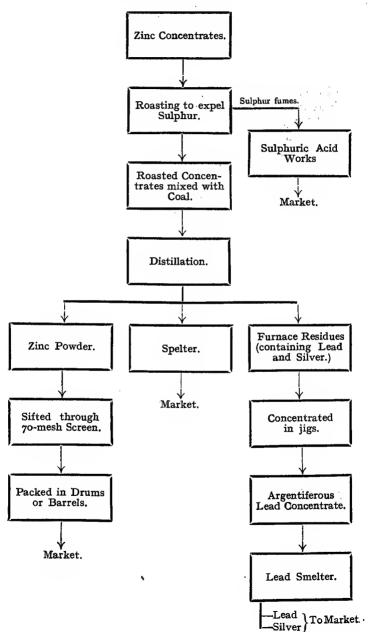
In addition to the home output, there is the proposed spelter production from Australia, which, as stated above, is to be imported to the extent of 45,000 tons per annum, and which would be of great assistance in making the total output approximately equal to the demand.

Climatic and labour conditions are, however, against any large extension of zinc distilling in Australia, and up to the present only the erection of small plant has been started there, and for a long time to come no appreciable tonnage of metal can be expected.

The Government has bought supplies of Broken Hill zinc concentrates, and many tons have been shipped to this country, but they are of no value to the country until they are turned into metal. The erection of works to effect this with all possible speed becomes imperative. It may be well to emphasise the fact that the complete treatment of these concentrates involves not only the production of zinc, they are also a potential source of sulphuric acid, and of lead and silver, and for economic reasons they should be worked to produce all these. The general method of treating the concentrates is shown in the accompanying flow sheet. (p. 208.)

To erect new zinc-smelting plant without proper provision for the utilisation of so valuable a product as the sulphur would undoubtedly be a serious mistake, and would greatly hinder the future development of the British zinc industry which is so urgently necessary, because it would not only waste a product of considerable value to the chemical industries, but would also deprive the zinc industry of a source of profit and increase the

FLOW SHEET SHOWING THE GENERAL METHOD OF TREATING AUSTRALIAN ZINC CONCENTRATES.



difficulty of meeting foreign competition. It is just the fact that this ore is a potential source of sulphuric acid which renders it necessary for the bulk of the concentrates to be shipped from Australia, where the market for acid is limited, to a country like Great Britain, with nine times the population of Australia and highly developed industries which can absorb the acid.

Probably one of the most difficult problems in connection with the utilisation of the sulphur is to decide on the most suitable location of the plant for roasting the ore. The Swansea district is one of the most favourably situated places in the world for the production of zinc and is the chief seat of the British industry, but it does not follow that the roasting of the ore for acid should necessarily be effected at the same place as the smelting of the roasted material for the metals. As already pointed out, it is not uncommon to find the roasting and the manufacture of sulphuric acid carried on in one district and the roasted ore smelted in another district where economic considerations render this course desirable. In treating the Australian concentrates in this country, therefore, it may be found, after a due consideration of all the circumstances, to be more suitable to roast the ore for acid at some centre connected with the chemical or galvanising industries, and to treat the roasted ore for zinc and its allied metals at Swansea or some other zinc-smelting centre, or even to extract the zinc in the same locality as that in which the sulphuric acid is made.

In adopting this latter course a considerable quantity of byproducts from galvanisers' works would be available in the immediate proximity of the projected smelting works, and the saving in freight alone on this material would probably be considerable. A most important element in favour of a scheme for the production of sulphuric acid from the roasting of concentrates is the keen interest shown by the leading manufacturers of sulphuric acid, who have been longing for an opportunity to adopt the Belgian blende roasting system in preference to the roasting of pyrites, which have been advancing in price considerably of late.

There is always an increasing demand for sulphuric acid in this country, especially for non-arsenical acid, as produced from zinc ores.

The whole question of the treatment of the Broken Hill zinc concentrates is, in view of the commercial and military

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value of zinc, of great importance, and the Government authorities have rightly decided that the handling of what is undoubtedly a great Imperial asset requires careful consideration. At the same time, there seems to be no reason why that consideration should be indefinitely deferred, and why, under proper safeguards to retain the control of this asset of the Empire, the treatment of the ore for its zinc and other valuable constituents should not be proceeded with without further delay, so that the country may be relieved of the necessity of importing spelter. The shortage of domestic zinc is bound to continue unless works are built capable of dealing with the zinc concentrates from Broken Hill. The war may yet last a long time, and it will scarcely be possible to hold up all trade and development questions until peace arrives.

The establishment in this country of a zinc-smelting industry on a scale commensurate with its needs is most urgently required.

There is no reason, if there is a proper application of organising ability, technical knowledge, perseverance and resourcefulness, why success should not be achieved.

We have in the country metallurgists with knowledge and experience of the very best Continental zinc-smelting plants and methods; we have the raw materials in ample quantity in the Empire; we have the demand for the metal, but we have not yet availed ourselves of these.

As Professor H. C. H. Carpenter <sup>1</sup> has well said, " the establishment in this country of a zinc industry on a scale commensurate with its needs would be an industrial victory of the first magnitude and it would remove a peril in which this country was placed by the outbreak of war, a peril which has been all too imperfectly realised, and should never be allowed to recur."

The urgent need is to make provision for the reconstruction that must follow on the declaration of peace, and in that reconstruction the development of the zinc industry holds an important place. There can be no doubt that further to neglect to respond to the urgent demands for a largely augmented output of zinc in this country will very seriously interfere with the progress of the non-ferrous metal industries, which have hitherto played so important a part in the industrial development, not only of this country, but of the British Empire, and are destined to be of much greater importance in the near future.

<sup>1</sup> Nature, 1916, vol. xcviii, p. 131.

### FUTURE OF THE ZINC INDUSTRY IN GREAT BRITAIN

The question as to what is going to be the future of the zinc industry in this country is one which has been exercising the mind of those who have the welfare of this industry at heart ever since the lamentable and dangerous situation at the outbreak of war was revealed. One cannot refrain from comparing the long delay in dealing with the question of the future development of the British zinc industry with the very expeditious manner in which the Royal Ontario Nickel Commission, appointed by the Ontario Government in September, 1915, dealt with the question of the nickel industry. Although many countries were visited. the Commissioners have, after a lapse of only eighteen months, presented their valuable and exhaustive report, which deals very fully with the nickel question, especially in relation to industry and trade, and will form a standard work of reference on nickel for many years to come. As the result of the recommendations of the Commissioners, extensive works are now being erected in Ontario for the treatment of the large quantities of ore found in the district, which have hitherto been mainly treated in the United States.

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